

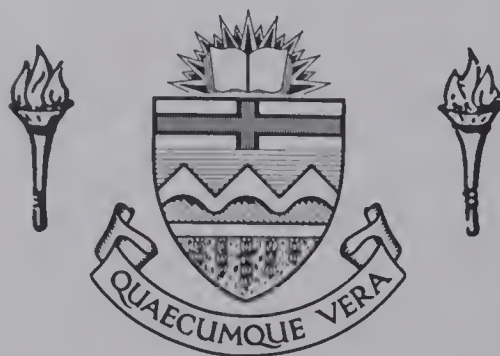
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NUCLEAR MAGNETIC RESONANCE STUDIES
OF
PENTAFLUOROPHENYL COMPOUNDS

BY



MICHAEL GORDON HOGBEN

A THESIS

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The undersigned certify that they have read and recommended to the Faculty of Graduate Studies for acceptance a thesis entitled

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PENTAFLUOROPHENYL COMPOUNDS

submitted by MICHAEL GORDON HOG BEN in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

The pentafluorophenyl group has been studied using nuclear magnetic resonance. The spectra of several pentafluorophenyl derivatives of widely varied chemical types have been analysed. Correlations are found among the nmr variables. In particular the coupling constant between ortho and para fluorines was found to give a straight line relationship with the chemical shift of the para fluorine. This is termed the $J_{24} - \phi_p$ relationship. Another meta fluorine coupling, the coupling constant between the two ortho fluorines, also forms a straight line relationship with the chemical shift of the para fluorine. These two correlations appear to be dependent upon the π donor-acceptor character of the substituent. This argument is then used to study the electronic interactions in selected series of organometallic and inorganic compounds. Interpretations of the bonding involved in these compounds are also given.

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CHAPTER I

INTRODUCTION

This chapter introduces the reader to the problem at hand, both to the experimental technique used in this work and the chemistry to which it is applied.

1. The Nuclear Magnetic Resonance Experiment. Nuclear magnetic resonance (nmr) was first observed in bulk matter in 1945. The first spectra with separate lines for chemically different nuclei in the same molecule were obtained for alcohols in 1951. Since that time it has become one of the most important analytical methods used in chemistry. Several textbooks are now available which provide more detailed accounts of its fundamentals and applications (1, 2, 3, 4). Nmr occurs when nuclei possessing magnetic moments are placed in a high magnetic field together with high frequency electromagnetic radiation. The most abundant isotope of hydrogen, the proton, has a magnetic moment of $\frac{1}{2}$. This makes it comparatively easy to observe and since hydrogen is present in many compounds, proton nmr has been the most extensively developed.

The spinning proton precesses around the direction of magnetic field in one of two possible orientations; aligned towards or against the field. These two states represent two quantum energy levels and the difference between the

energy levels is related to the transition frequency. This difference in energy is proportional to the applied magnetic field and is characteristic of each isotope at that field. Irradiation of the nuclei at the appropriate frequency, which is the same as the classical precessional frequency, causes the net resultant magnetic moment of the nuclei to move away from the direction of the magnetic field. The induced transitions then absorb some of the energy of the irradiation.

Although the magnetic field is kept constant, each nucleus in a molecule will experience a slightly modified field. This is because of the diamagnetic contribution of the surrounding electrons in which a small magnetic dipole moment is induced against the main field. Thus if the nucleus is heavily 'shielded' by electrons, the main field must be increased to offset that produced by the electrons so that the effective magnetic field at the nucleus is at the correct strength for resonance. Thus an upfield shift indicates a high density of electrons around the nucleus. Conversely a down-field shift is the result of the nucleus being "deshielded". Since magnetic field and the frequency are directly proportional the upfield shift can be expressed in gauss or, as is used in practice, cycles per second (cps). This shift is termed the chemical shift, first propounded as a term of annoyance by physicists who might have preferred that

the resonance frequency be constant for all nuclei of the same type. Although diamagnetism is the main cause of chemical shifts in proton nmr, it should be noted that second order paramagnetic effects (large down-field shifts) predominate in fluorine nmr. Even larger down-field shifts are possible in molecules with unpaired electrons near the nucleus. Magnetic anisotropy in the molecule will also cause both upfield and downfield shifts depending on the position of the nucleus with respect to the anisotropy. Chemical shifts are proportional to the overall magnetic field. The chemical shift is expressed in parts per million, ppm, which is therefore constant for all fields.

One other means whereby the frequency (or field) required to achieve resonance is modified is termed spin-spin interaction. It is found that the signal for any one group of chemically different nuclei is often split into a multiplet of lines. This arises from an interaction between neighboring nuclear spins through an indirect coupling mechanism via the electrons in the molecule. The magnitudes of these spin interaction energies are called coupling constants and are expressed in cycles per second (cps). Coupling constants are independent of the magnetic field, which differentiates them from chemical shifts.

Using Pople's notation, chemically different groups of nuclei in a molecule are identified by different letters

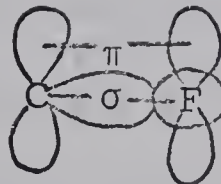
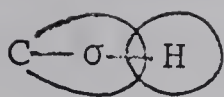
of the alphabet. Hence a compound with two groups of hydrogen, each with two nuclei, is designated A_2B_2 . When the chemical shifts of each group of nuclei are well separated, the spectra is designated A_2X_2 . If the molecule has symmetry such that the nuclei are magnetically unequivalent although chemically equivalent, it is designated $AA'XX'$. Magnetic non-equivalence requires the coupling of, say, one of the A nuclei to one of the X nuclei to be different to the coupling to the other X nucleus (i.e. $J_{AX} \neq J_{AX'}$). Provided the difference in the chemical shifts between the nuclei is large compared to the coupling constant and provided symmetry in the molecule does not cause magnetic non-equivalence, the spectra are termed "first-order" and are relatively simple to interpret. When these conditions do not exist, second order effects predominate and complicate the spectra.

Fluorine nmr, although not so well developed experimentally, is comparable and in some aspects advantageous compared with proton nmr. Both chemical shifts and coupling constants are larger in fluorine nmr than for the equivalent proton spectra. The ratio of chemical shift to coupling constant is greater thus reducing second order effects. Fluorine-19 is the only naturally occurring isotope of this element and has a spin moment of a half. Consequently it does not suffer from quadrupole effects. Although slightly less sensitive and easier to saturate than hydrogen, fluorine resonance is relatively easy to

observe by modifying proton nmr instruments.

For hydrogen, spectra are usually recorded at 100 Mc/s or 60 Mc/s which correspond to magnetic fields of 23,500 gauss and 14,000 gauss. Fluorine will resonate using these magnetic field strengths at frequencies of 94.1 Mc/s and 56.4 Mc/s. The resolution of these instruments can be extremely good. Our studies showed that under favorable conditions, the resolution was 0.2 cps using the 56 Mc/s instrument. If the same resolution, 1 in 300,000,000, was transferable to telescopic systems, this would be equivalent to separately identifying two astronauts only five feet apart on the moon's surface! The best results obtained in proton nmr would be equivalent to separating the astronaut's two eyes.

2. The use of fluorine nmr of the pentafluorophenyl group in determining substituent effects. Fluorine, like hydrogen, is monovalent and can be substituted for hydrogen in a variety of compounds. A principal difference between fluorocarbon and hydrocarbon chemistry is that the high electronegativity of fluorine causes the fluorocarbon group to behave as an electron accepting group. In contrast to hydrogen, fluorine can also interact with π orbitals in conjugated carbon systems through the use of its filled p orbitals as shown schematically below:



In fluorine-containing conjugated molecules, differences in F^{19} nuclear shielding are determined largely by the π -electron charge density and the C-F bond orders (5). Hence it was anticipated that F^{19} nmr of fluorines in pentafluorophenyl derivatives would indicate the changes in π -electron density resulting from different substituents attached to the pentafluorobenzene ring.

The following survey includes nearly all the available F^{19} nmr data of the pentafluorophenyl group published to date. Although nmr has proved to be a most useful method in the determination of the structure of many compounds, its application to bonding, in particular, the study of substituent-benzene ring interactions has not been so well developed, with one exception. R. W. Taft and coworkers (6) in what is probably the most voluminous, the most complete and the most rewarding study in this field, found that the fluorine nmr of the two series of para and meta fluorophenyl derivatives could be related to the resonance and inductive contributions of the substituent effects. They were able to correlate their results with those found from reactivity studies of the

substituent as first developed by Hammett (7). This technique has been applied to problems in organometallic chemistry by Parshall who studied the metal-ligand (X) interaction in the two series of para and meta $\text{FC}_6\text{H}_4\text{Pt}^{\text{II}}[\text{P}(\text{Et})_3]_2\text{X}$ compounds. However, the problem of preparing two series of compounds and the inherent dangers in assuming that the substituent acts in the same way for each series have led chemists to seek other methods in the study of substituent effects by nmr.

Although proton nmr has been extensively developed, its application to benzene interactions has been limited by the closely spaced chemical shifts of the ortho, meta and para protons. The second order interaction can be interpreted with difficulty by a complete analysis of the type AA'BB'C. However Spiesecke and Schneider (8) analysed the proton nmr of a few monosubstituted benzenes by assigning and measuring the proton signals with the aid of deuterium substitution. This work also cites references for the 'complete analysis' approach.

Spiesecke and Schneider (8) also measured the C^{13} nmr of the same compounds using that element in its natural abundance. Because of the low abundance C^{13} atoms ($\sim 1\%$), concentrated solutions were used and solvent effects were more noticeable. However, several studies have been made using C^{13} nmr (9,10,11).

Boron nmr has also been used to demonstrate substituent effects on the electron densities on the benzene ring in a

study of para-substituted phenylboronic acids (12).

The use of F^{19} nmr of pentafluorophenyl derivatives has been investigated only recently due to the new developments in synthetic pentafluorophenyl chemistry together with commercial availability of pentafluorophenyl reagents. Chemical shifts alone may be measured without the need of a full analysis and several organometallic compounds have been studied this way (13,14). Using common organic substituents, both chemical shifts and coupling constants have been derived, the chemical shifts being related to π -electron charge densities and C-F bond orders (15); to previously deduced Taft functions (16); and to metal-ligand interactions (17). Fluorine nmr data are also found in the literature for individual compounds (18,19,20) which are useful for future evaluation or for giving a clearer understanding of the spectral analysis (21). Correlations of coupling constants and chemical shifts with Hammett-Taft functions have been attempted with varying degrees of success (22). However, the extensive data resulting from the present work have revealed new correlations among these parameters which constitute the subject of this study.

This thesis describes the measurement, analysis and compilation of F^{19} nmr parameters for the pentafluorophenyl system. It describes the correlations found among these nmr parameters and also correlations of these parameters

with substituent effects. A proposal is formulated that the π electron donor-acceptor character of the substituent is related to its position on the graph of its coupling constant between the ortho and para fluorines plotted against the chemical shift of the para-fluorine. In the light of this proposal, selected series of compounds are examined and the electronic interactions within the molecule are compared with current concepts of bonding.

CHAPTER II

EXPERIMENTAL

This chapter describes the experimental techniques of the preparation, measurements, spectroscopic and statistical analysis used to present the results of the following chapter.

1. Preparation and source of compounds studied. All pentafluorophenyl reagents used in this work were obtained from Imperial Smelting Corporation. The boron halides and CFCl_3 were obtained from the Matheson Co. Inc., and other chemicals from the usual commercial sources. The boron halide and hydrogen chloride complexes of $\text{C}_6\text{F}_5\text{P}(\text{C}_6\text{H}_5)_2$ and $\text{C}_6\text{F}_5\text{CN}$ were prepared using conventional high vacuum technique by distilling an excess of the gas directly into the nmr tube containing a degassed benzene solution of the pentafluorophenyl compound and hexafluorobenzene. In the case of $\text{C}_6\text{F}_5\text{P}(\text{C}_6\text{H}_5)_2\text{-BCl}_3$, the nmr spectra were recorded immediately upon warming since the complex crystallized out within a few hours. The crystalline complex was isolated and recrystallized from methylene chloride.

Anal. Calcd for $\text{C}_{18}\text{H}_{10}\text{BCl}_3\text{F}_5\text{P}$: C, 46.1; H, 2.2.
Found: C, 46.8; H, 2.3. (A. Bernhardt 25528/68)

Although the complex could not be redissolved to get reasonable spectra, very small peaks appearing at the correct chemical shifts were sufficient to distinguish

the compound from the HCl adduct.

The C_6F_5CN complexes with BF_3 , BCl_3 , and BBr_3 were not isolated or characterized due to dissociation of the adducts. For this reason, some caution is necessary in interpreting the spectra of the C_6F_5CN complexes. All other new compounds prepared were characterized either by elemental or by mass spectral analysis.

The various phosphines and the rest of their complexes were prepared in this laboratory by reaction of pentafluorophenyllithium and the appropriate phosphorus chloride and subsequent reaction with the metal carbonyl (23). The various pentafluorophenyltin compounds were prepared in this laboratory by the reaction of pentafluorophenyllithium with the appropriate halotin compound (24). The pentafluorophenoxy, pentafluorothiophenoxy and pentafluoroaniline derivatives were also prepared in this laboratory by the reaction of the appropriate organometallic halide with pentafluorophenol or its sodium salt, pentafluorothiophenol, or N-lithio pentafluoroaniline (25). Pentafluoro-N,N-dimethylaniline was prepared by refluxing pentafluoroaniline with aqueous formic acid and aqueous formaldehyde after the manner of Allen, Burdon and Tatlow (26).

2. Nmr Measurements. All spectra recorded for this work were measured on Varian spectrometers at the University of Alberta. Although the present facilities (fall 1967) include an A56/60 spectrometer which records spectra with all the ease, routine and speed of proton spectra, all the compounds presented in Chapter III were re-recorded when fluorine nmr, particularly the instrumentation, was at an earlier stage of development. Little had been published on solvent effects in fluorine nmr until recently (27) and standardization of references and scales in reporting F^{19} chemical shifts has still to become effective. Spectrometers were merely adapted from proton work incurring problems due to the large range of chemical shifts found for fluorine nmr. During the course of this work a number of techniques were devised. These techniques generally gave similar accuracy but the later methods gave considerable improvement in the speed with which good high resolution spectra could be produced.

The HR mode. The first experiments were performed on an HR 100 spectrometer, modified to observe fluorine nuclei at the same field by retuning the circuits to accept the new frequency, 94.1 Mc/s. The spectra were scanned by 'field sweep' which, because of the non-linear and irregular change in field, required averaging of several sweeps upfield and downfield to accurately locate line

positions. The wide range of chemical shifts (ie. 180 ppm = 17,000 cps) made it necessary to adjust the fine tune (curvature, Y and phase) for each multiplet. This could only be done by finding a sharp line of 'normal' shape within the multiplet and tuning to the best shape, a process which is best described as subjective in nature. Line positions were obtained by 'bracketing' using sidebands of the reference produced by an audio-oscillator. Double irradiation was attempted but decoupling was unsuccessful, no doubt because of the difference in line shape between multiplets many kilocycles apart. The only advantage of this instrument was that the larger field and higher frequency meant a signal to noise ratio approximately three times higher than that found on the 56.4 Mc/sec instrument.

HA mode Stage I. Nearly all compounds in Chapter III were analysed on the HA 60 instrument converted to 56.4 Mc/sec. The HA system 'locks' on to the reference and so only one sweep is necessary for each spectrum. The best resolution is found by adjusting the fine tune controls until a maximum reading of the shim system is found. This process is considerably better and quicker than the equivalent operation in HR mode. Double irradiation was successful using this technique. The only disadvantage was that the machine did not adequately cover the wide

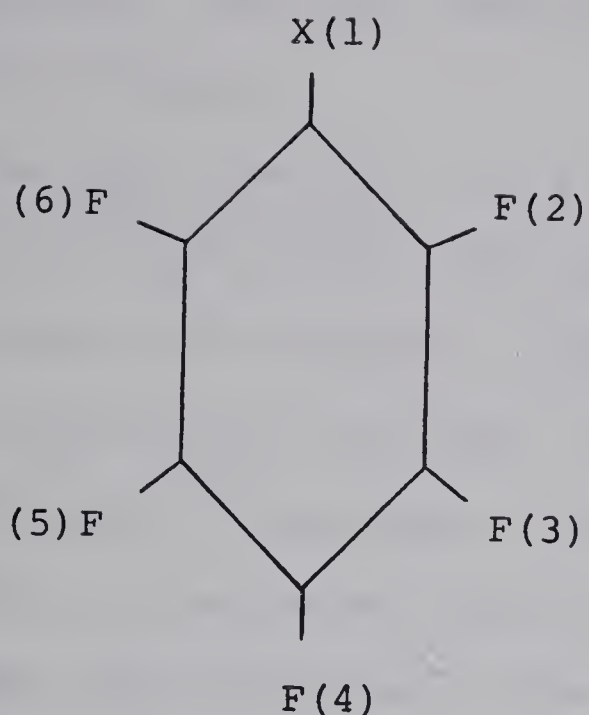
range of chemical shifts which caused the ortho spectra to be recorded at low expansion and sometimes not at all. HA mode, Stage II. The difficulty in obtaining a long range lock as mentioned above was resolved during this study by disabling the normal 2500 cps oscillator and substituting a Hewlett Packard 241A oscillator by which means the offset could be increased to encompass all possible fluorine shifts. The HA field frequency lock system was attempted at 94.1 Mc/sec but the fluorine probe could not be retuned as well as on the 60 Mc/sec instrument and so caused instability in the oscillator. This then required the fine control to be adjusted every 30 seconds which was shorter than the sweep time (generally 500 sec). Using the above methods, nearly all the spectra were recorded by the author although a few were run by Mr. Glen Bigam of this laboratory. The A56/60 spectrometer was used only for the 12 additional compounds presented in Chapter IV.

Measurement of spectrometer output. A machine was designed by the author and constructed by the Machine Shop which measured the distance between two maxima on the chart paper to a greater accuracy than the output of the spectrometer justified. The machine could be set on any one line to a precision of 0.04 mm. Measurements were taken to 0.1 mm. Since the spectra were recorded at 100 cps sweepwidth

covering 500 mm of paper an error of ± 0.1 mm was equivalent to ± 0.02 cps. This was within the accuracy required for our results since coupling constants are quoted to 0.1 cps and chemical shifts to 5 cps (0.1 ppm).

The spectra were recorded using 20 - 30% (v/v or w/w) solutions in benzene except for some of the phosphine complexes, especially those of the metal carbonyls, which were sparingly soluble and were measured as saturated solutions. Hexafluorobenzene was used as internal reference and chemical shifts are presented relative to CFCl_3 by adding 163.0 ppm (see Chapter III). When the reference obscured sample absorption, as in the case of $\text{C}_6\text{F}_5\text{NH}_2$, boron trifluoride etherate in a capillary was used as the "locked in" signal and chemical shifts of the observed multiplets relative to CFCl_3 were established by comparison of and measured relative to both standards. The temperature of measurement ranged from 30 °C on the HA 56.4 to 40 °C on the A56/60.

3. Spectral Analysis. The analysis of the pentafluorophenyl group was accomplished by treating the system as AA'KXX'. Figure 1 shows the nomenclature used for identifying the fluorines on the benzene ring, their chemical shifts and coupling constants. Four more parameters (K, L, M and N) are also defined since these are used in the analyses. It is assumed in this section that coupling



X is the substituent atom

Chemical shift of F(2) and F(6)

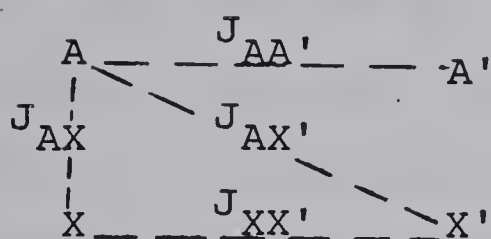
$$= \phi_o$$

Chemical shift of F(3) and F(5)

$$= \phi_m$$

Chemical shift of F(4)

$$= \phi_p$$



note: $J_{AA'} \equiv J_{26}$

$$J_{XX'} \equiv J_{35}$$

$$J_{AX} \equiv J_{23} (=J_{56})$$

$$J_{AX'} \equiv J_{25} (=J_{36})$$

The analysis parameters K, L, M, N are defined as follows:

$$K = J_{AA'} + J_{XX'}, \quad L = J_{AX} - J_{AX'}$$

$$M = J_{AA'} - J_{XX'}, \quad N = J_{AX} + J_{AX'}$$

Figure 1. Explanation of nomenclature used in labelling chemical shifts and coupling constants of the pentafluorophenyl group.

constants are small compared to separations in chemical shifts. This was true for all analyses undertaken in this thesis.

The para spectrum. In a complete analysis of the nmr of the C_6F_5 -group, the para-fluorine spectrum is the first to be analysed. Figure 2 shows an example,

$C_6F_5P(C_6H_5)_2$, of this. The spectrum is a triplet of triplets of doublets. The doublets (J_{14}) are due to first order interaction with the substituent phosphorus atom.

When the substituent does not have atoms with magnetic moments or when substituent-ring interactions are negligible, the doublets are collapsed into single peaks as in the cases of C_6F_5COCl and $C_6F_5NH_2$ (Figures 3 and 4). Of the other couplings J_{34} varies little from 20 cps although J_{24} may vary from zero to 8 cps - see Chapter III. Minor second order interactions may show in the central triplet as has been shown recently (28). All measurements of J_{24} were taken from the outer triplets and averaged before presentation in the Tables of Chapter III. The chemical shift was taken from the position of the central peak.

The meta spectrum. The meta-spectrum in aromatic systems is always complicated by its symmetry. Although the meta fluorines are chemically equivalent they are magnetically unequivalent. By this we mean that coupling across the ring between the ortho and meta fluorines ($J_{AX'}$) is not

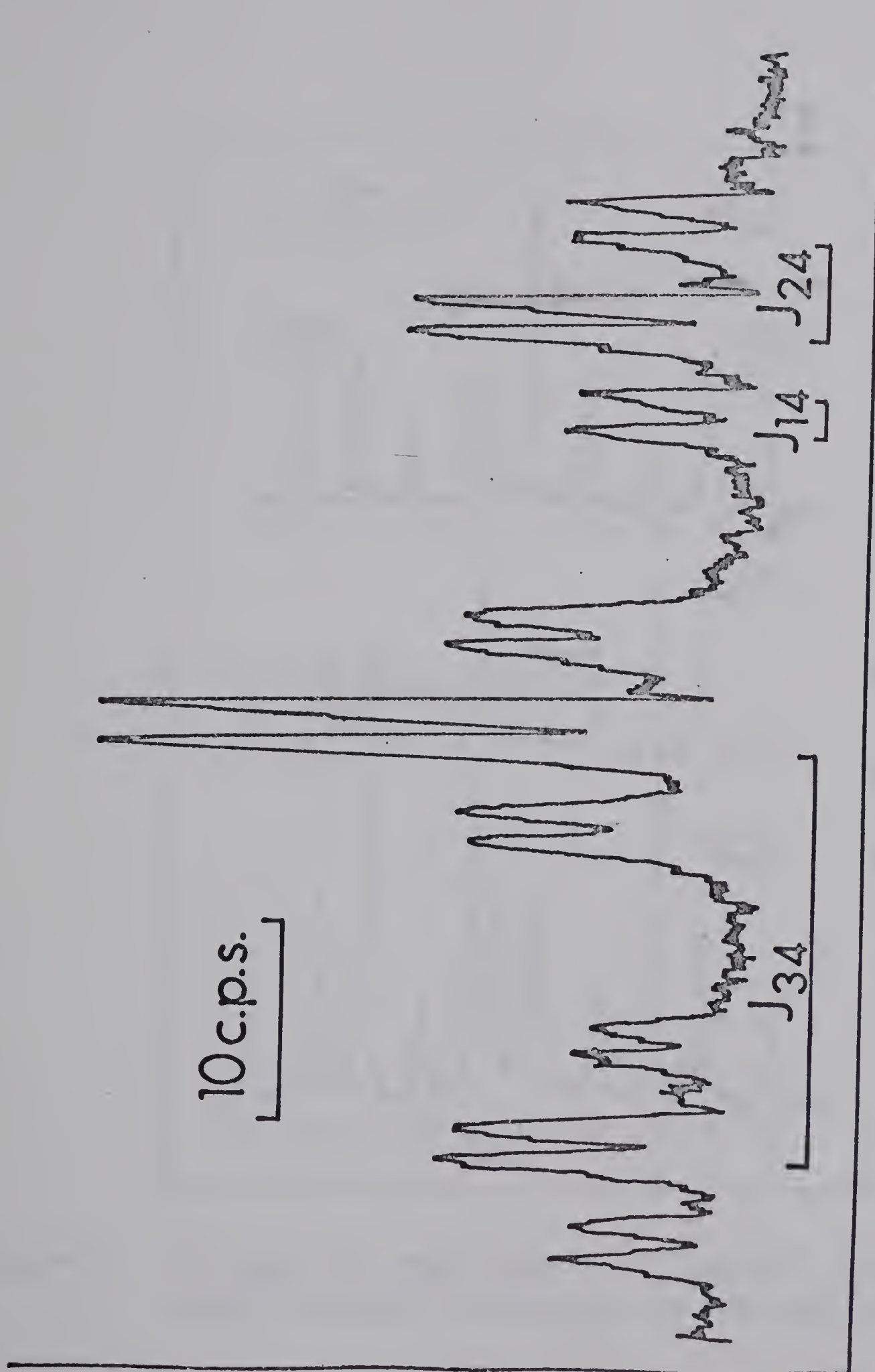


Figure 2: Typical spectrum of a para fluorine; of $\text{C}_6\text{F}_5\text{P}(\text{C}_6\text{H}_5)_2$

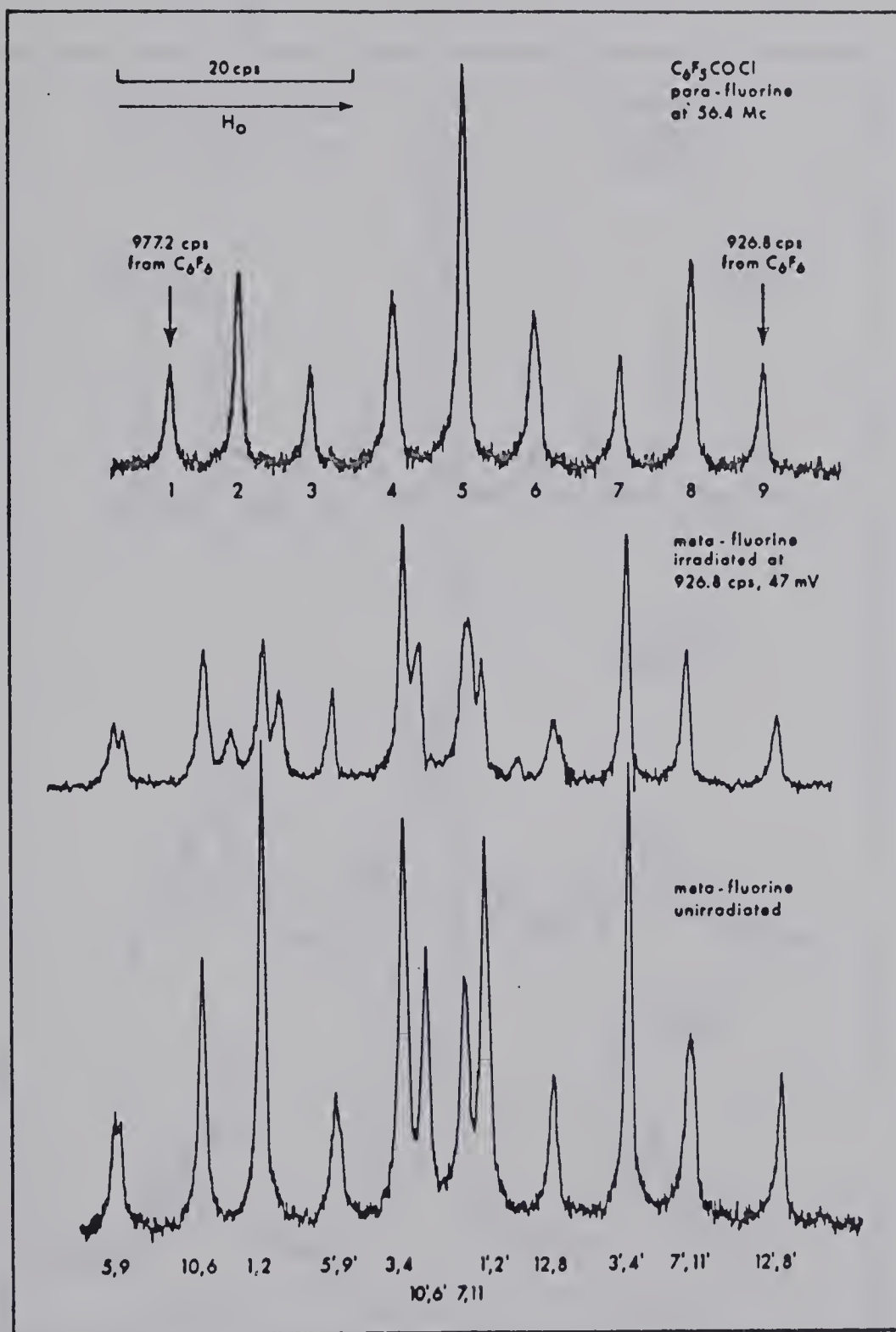


Figure 3. The para and meta spectra of C_6F_5COCl , showing the effect of double irradiation on the meta spectrum.

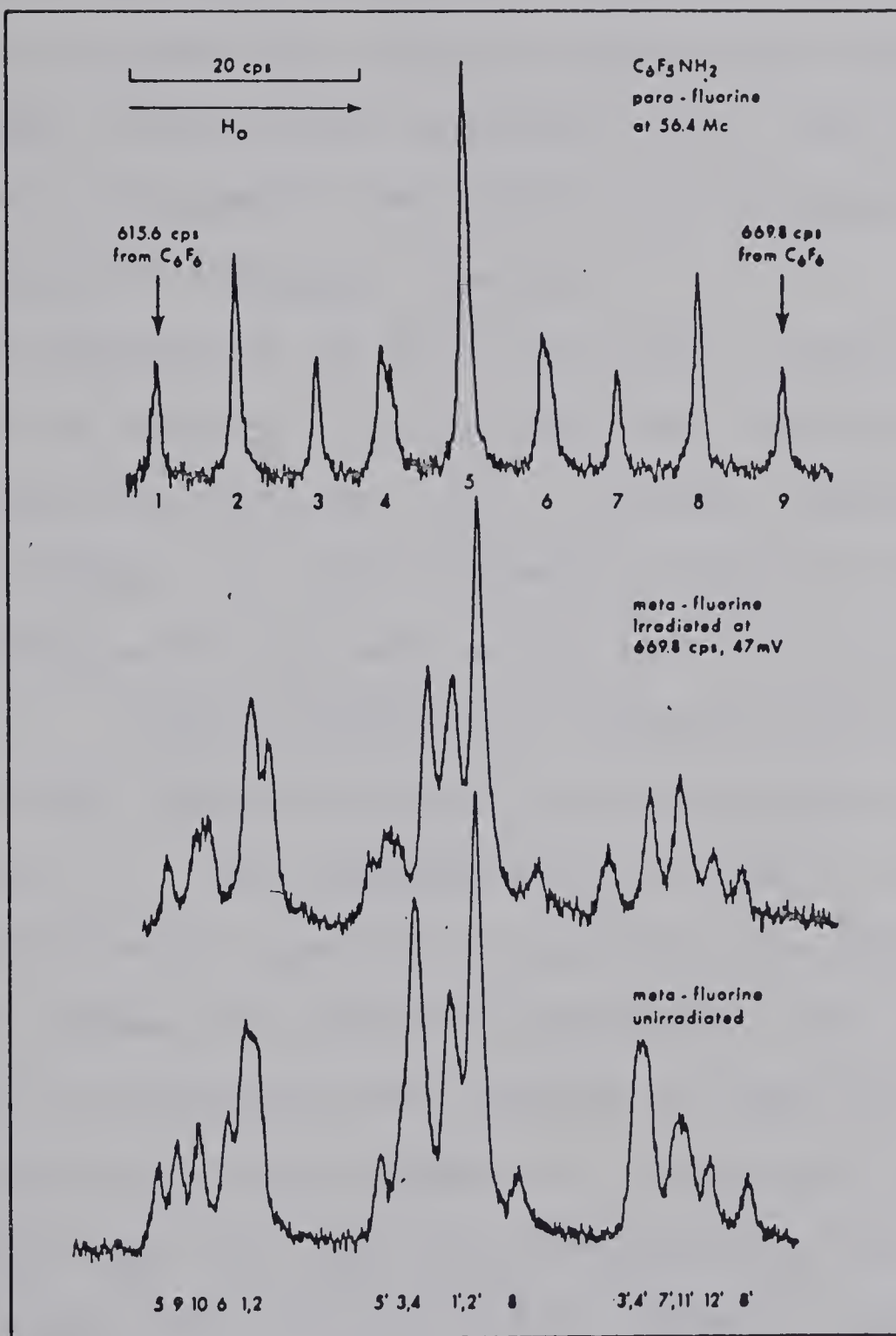
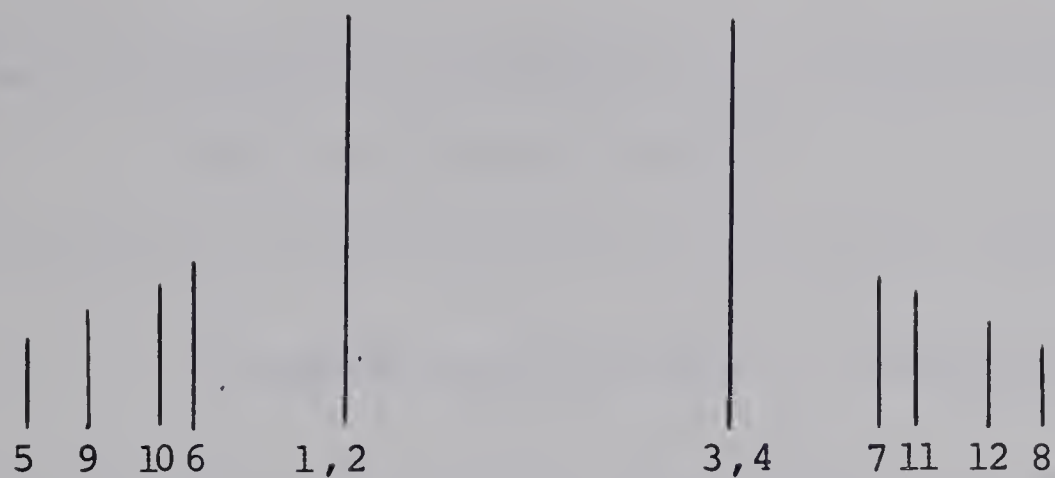


Figure 4. The para and meta spectra of $C_6F_5NH_2$, showing the effect of double irradiation on the meta spectrum.

the same as coupling between adjacent ortho and meta fluorines (J_{AX}). The spectra are also complicated by coupling to the para fluorine. Therefore the spectra have been analysed by a technique which has recently been termed "sub-spectral analysis" (28). Thus the meta spectrum is analysed as two AA'XX' systems separated by the coupling to the para fluorine.

The analysis of the AA'XX' has been treated in the standard nmr texts (3, 4) by using the technique of Grant, Hirst and Gutowsky (29). Using the labelling shown in Figure 5, the energies and relative intensities of transitions for one half of the AA'XX' are given in Table I. A half spectrum of a typical AA'XX' system derived from pentafluorophenyl nmr measurements is given in Figure 5. The parameters K, L, M and N, can be extracted from the spectrum by measuring the separation (in cps) between the various transitions. This can be verified by subtracting the energies of each pair of transitions as listed in Table I. The actual coupling constants, J_{26} , J_{35} , J_{23} ($=J_{56}$) and J_{25} ($=J_{36}$) can then be calculated from K, L, M and N. Aromatic fluorine coupling constants differ from aromatic proton coupling constants in that coupling across the ring (J_{AX}) is of opposite sign to the coupling between adjacent fluorines (J_{AX}) whereas the two coupling constants are of the same



N is the separation of 1,2 and 3,4.

K is the separation of 5 and 6; 7 and 8.

M is the separation of 9 and 10; 11 and 12.

L is derived from $(X^2 - K^2)^{\frac{1}{2}}$

where X is the separation of 5 and 7; 6 and 8

or from $(Y^2 - M^2)^{\frac{1}{2}}$

where Y is the separation of 9 and 11; 10 and 12.

Figure 5. Interpretation of half spectrum of a typical AA'XX' system.

TABLE I

Energies and Relative Intensities of A Transitions
for Four Nuclei AA'XX' ^a

Line	Energy relative to ν_a	Relative Intensity ^b
1	$\frac{1}{2}N$	1
2	$\frac{1}{2}N$	1
3	$-\frac{1}{2}N$	1
4	$-\frac{1}{2}N$	1
5	$\frac{1}{2}K + \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}}$	$\sin^2 \theta_s$
6	$-\frac{1}{2}K + \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}}$	$\cos^2 \theta_s$
7	$\frac{1}{2}K - \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}}$	$\cos^2 \theta_s$
8	$-\frac{1}{2}K - \frac{1}{2}(K^2 + L^2)^{\frac{1}{2}}$	$\sin^2 \theta_s$
9	$\frac{1}{2}M + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\sin^2 \theta_a$
10	$-\frac{1}{2}M + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\cos^2 \theta_a$
11	$\frac{1}{2}M - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\cos^2 \theta_a$
12	$-\frac{1}{2}M - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\sin^2 \theta_a$

^a As given by Pople, Schneider and Bernstein (3).

^b Defined by $\cos 2\theta_s : \sin 2\theta_s : 1 = K:L:(K^2 + L^2)^{\frac{1}{2}}$
Defined by $\cos 2\theta_a : \sin 2\theta_a : 1 = M:L:(M^2 + L^2)^{\frac{1}{2}}$

sign for protons. This alters the spectra so that lines 1,2 and 3,4 are inside the quartets 5, 6, 7, 8 and 9, 10, 11, 12 for fluorine although outside for protons. This sign dependency is the only one that is recognizable in AA'XX' spectra. The shape is not influenced by the signs of the other coupling constants. It should also be noted that the magnitudes of $J_{AA'}$ ($=J_{26}$) and $J_{XX'}$ ($=J_{35}$) are indistinguishable. This is also true for J_{AX} ($=J_{23}$) and $J_{AX'}$ ($=J_{25}$) although the larger coupling (~ 20 cps) is assigned to J_{23} since this is always close to the value found for J_{34} , the other coupling between adjacent fluorines.

The meta spectrum displays two overlapping AA'XX' half spectra, separated by J_{34} . These are separated by using the value of J_{34} found from the para spectrum. Figure 6 shows the observed meta spectrum together with the upfield half spectrum from the AA'XX' system for $C_6F_5P(C_6H_5)_2$. The spectrum is further modified by first order interaction from the phosphorus, (J_{13}), giving close doublets to every calculated line from the AA'KXX' system. It should be noted that although the labelling of lines in the meta spectrum is consistent with the literature (3), the use of 'primed' numbers, (ie. 5', 9', 10', 6' etc.) is not and has been reserved for the upfield half of each meta spectrum resulting from coupling to the

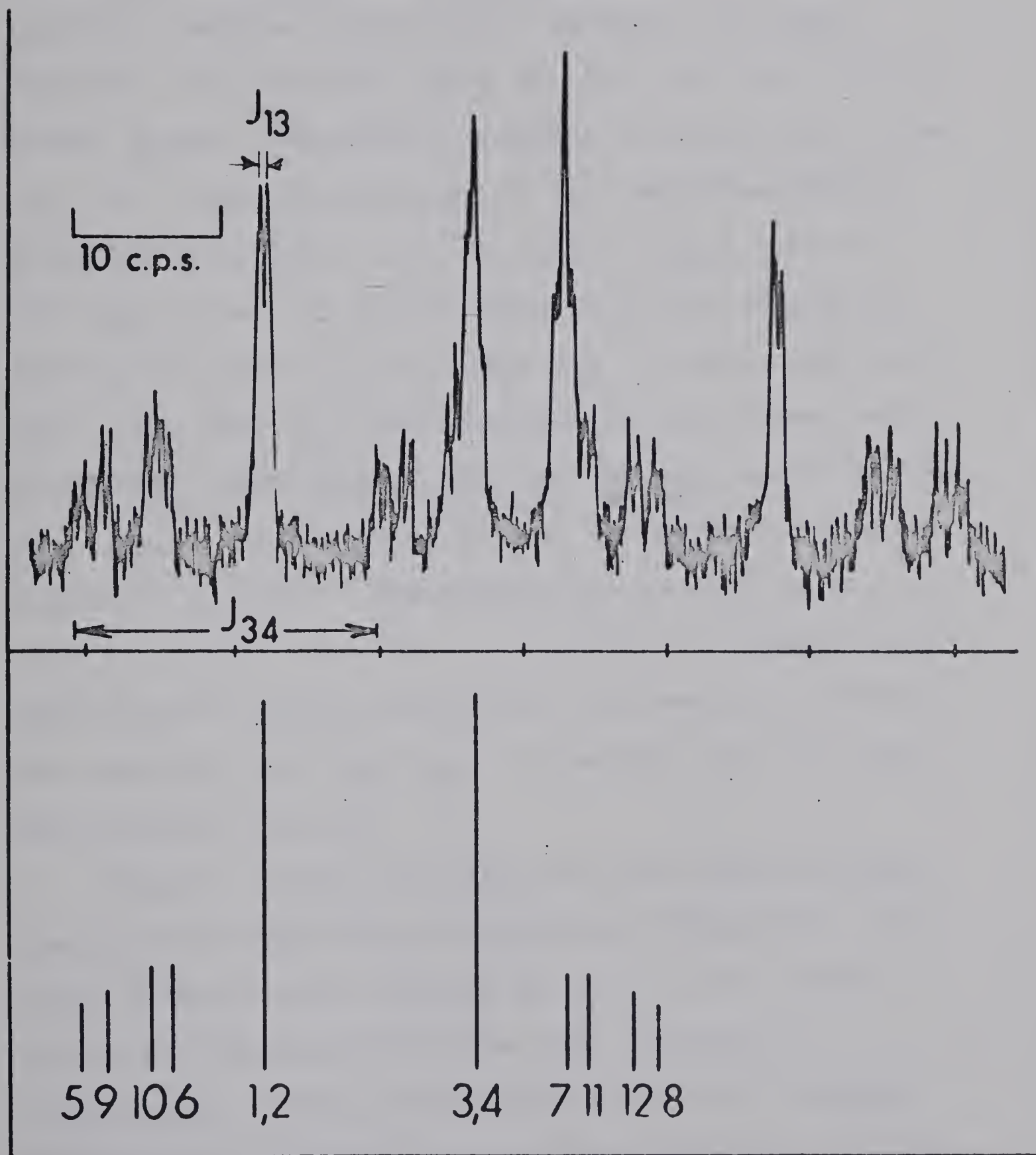


Figure 6: Observed and calculated spectrum for the meta upfield half spectrum for $C_6F_5P(C_6H_5)_2$.

para fluorine.

The ortho spectrum. The ortho spectrum is treated in exactly the same manner as the meta spectrum. Sub-spectral analysis allows us to 'uncouple' the para fluorine, the remainder being the low field half of the AA'XX' system. Except for coupling to substituent atoms (J_{12}) all coupling constants of the pentafluorophenyl group are obtainable from the meta and para spectrum. The ortho spectrum also suffers from more accidental overlap of spectral lines since J_{24} is always substantially less than J_{34} , and couplings to substituent atoms are usually much greater than for the meta spectrum (ie. $J_{12} > J_{13}$). As mentioned before, the orthospectrum was difficult to observe experimentally since it occurs outside the normal range of a converted proton spectrometer. Therefore the ortho spectrum was not examined in detail; the chemical shift and J_{12} , if possible, were the only data usually recorded.

Figure 7 shows the calculated and observed ortho spectra for complexed and uncomplexed phosphines. The upper diagram shows the half spectrum of the AA'XX' system as calculated from the meta spectrum of $C_6F_5P(C_6H_5)_2$. First order interaction with the para fluorine (J_{24}) yields the theoretical spectrum if coupling to the phosphorus (J_{12}) is zero. Figure 7c

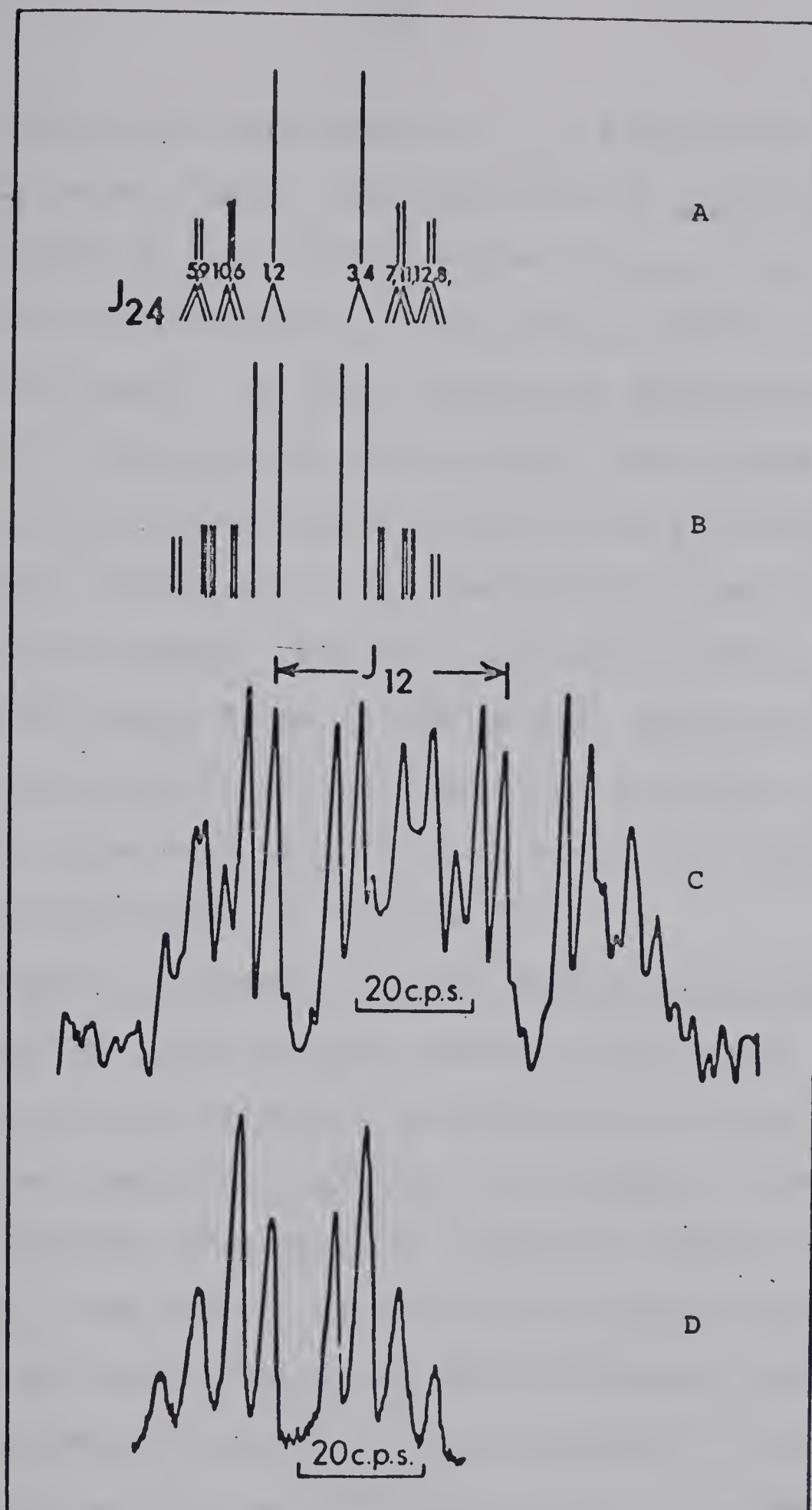


Figure 7: a, half spectrum of AA'XX' derived from meta spectrum.

b, theoretical ortho spectrum $J_{12} = 0$

c, observed spectrum of $C_6F_5P(C_6H_5)_2$

d, observed spectrum of $C_6F_5P(C_6H_5)_2Mo(CO)_5$

shows the observed spectrum and J_{12} is determined by inspection to be 39 cps. The spectrum for $C_6F_5P(C_6H_5)_2Mo(CO)_5$ should be very similar since all J_{F-F} 's for the two compounds are comparable in magnitude. However it can be seen from Figure 7d that coupling to phosphorus is not resolved. Since J_{24} is unfortunately very close to the separation of the groups of lines in the low field half of the AA'XX' system, the forty theoretical lines fall into eight diffuse peaks. Only the two inner lines are derived from single lines in the AA'KXX' system and since these are not split in the phosphine complexes, J_{12} must be taken to be less than the line width (1.8 cps). This is discussed further in Chapter III.

Determination of signs of J_{24} by double irradiation. While the coupling constants and chemical shifts were being compiled, it became necessary to determine the sign of J_{24} in the two compounds, C_6F_5COCl and $C_6F_5NH_2$. Since this is not apparent from spectral analysis, double irradiation was used. The spectra of these two compounds were verified to be correct using the TWOSUM computer program, which has been developed in the Department of Chemistry, University of Alberta, Edmonton by Drs. G. R. Demaré, J. S. Martin and F. W. Birss. TWOSUM is based on NMRIT and NMREN, two programs by Ferguson and Marquardt (30). This program gave the transitions and associated energy

levels that are shown in Table II. The transitions are given for two calculations using the same chemical shifts and coupling constants except that the relative sign of J_{24} is changed in the second case. Comparisons of these computations with the observed spectra shown in Figures 3 and 4, shows that if each compound is irradiated at a frequency corresponding to the line to highest field in the para spectrum (line 9 in the para spectrum), changes will occur in the meta spectrum that will be sensitive to the relative sign of J_{24} . If the sign of J_{24} is the same as J_{23} , line 9 of the para spectrum will involve energy levels 1 and 4. These energy levels are also found in the meta spectrum at lines 3,4 and 3',4'. In the case of $C_6F_5NH_2$, lines 3,4 and 3',4' were the only lines affected by double irradiation. Lines 3,4 and 3',4' are each composed of two transitions. One of these transitions did not involve an energy level common to line 9 of the para spectrum and therefore remained unaffected. The other transition separated into two transitions of decreased intensity placed to each side of the original line. Thus the overall effect is that irradiating $C_6F_5NH_2$ with a frequency corresponding to line 9 in the para spectrum caused lines 3,4 and 3',4' to halve their intensities and produced two extra lines on either side of the original line. This constitutes case (a) in Table II.

TABLE II

Energy Levels computed for transitions in the Para and Meta-fluorine spectra of pentafluorobenzoyl chloride.^a

Line ^b		Energy levels for each transition	
<u>Para</u> -spectrum		J ₂₄ same sign as J ₂₃	J ₂₄ opposite sign to J ₂₃
H _O ↓	1	29-32	16-26
	2	24-30, 25-31	24-30, 25-31
	3	16-26	29-32
	4	19-27, 18-28	6-14, 5-15
	5	11-20, 13-22, 10-21, 12-23	10-21, 12-23, 11-20, 13-22
	6	6-14, 5-15	19-27, 18-28
	7	7-17	1-4
	8	2-8, 3-9	2-8, 3-9
	9	1-4 (a)	7-17 (b)
<u>Meta</u> -spectrum		For Both cases of sign	
H _O ↓	5,9	9-21, 23-30	
	10,6	22-31, 8-20	
	1,2	(b) 17-27, 27-32	
	5',9'	3-10, 12-24	
	3,4	(a) 4-14, 14-26	
	10',6'	13-25, 2-11	
	7,11	9-22, 20-30	
	1',2'	(b) 19-29, 7-19	
	12,8	21-31, 8-23	
	3',4'	(a) 6-16, 1-6	
	7',11'	3-13, 11-24	
	12',8'	10-25, 2-12	

^a Symbols (a) and (b) refer to energy levels common to both para and meta spectra, depending on the sign of J₂₄ (see text).

^b The same numbering of lines is also used in Figures 3 and 4.

Irradiating $\text{C}_6\text{F}_5\text{COCl}$ at a frequency corresponding to line 9 of the para spectrum caused lines 1,2 and 1',2' to be affected as shown in Figure 4. This constitutes case (b) in Table II.

Since J_{23} is considered to be negative (21) and J_{23} changes little with substituent, it is concluded that J_{24} was of different sign for $\text{C}_6\text{F}_5\text{COCl}$ ($J_{24} > 0$) as compared to $\text{C}_6\text{F}_5\text{NH}_2$ ($J_{24} < 0$).

4 Statistical analysis of results. A statistical analysis of the chemical shifts, coupling constants and Hammett-Taft substituent functions was undertaken to determine whether correlations existed between these variables. A computer program was developed which quantitatively estimated the likelihood that a meaningful straight line relationship existed between any two variables. An option in the program allowed one variable (Y) to be plotted against a predetermined combination of two other variables (eg. $(X_1) + K(X_2)$, where K is predetermined) or even the best combination of X_1 and X_2 . In the latter case the program calculates the value of K that gives the closest approximation to a straight line.

The program, designated XLSQ3, was written in Fortran IV for operation under the LBJOB monitor. It was processed using the IBM 1401/7040 computer at the University of Alberta, Department of Computing Science. The Fortran listing is given in Appendix A. Salient features of the input and output follow.

The input consisted of a control card followed by the input data. An example of the input data is given in Figure 8. Each compound is identified by the chemical formula of its pentafluorophenyl substituent (IDENTITY) and the source of the data (REF). Each compound has the space for twelve parameters which were usually three

REF	IDENTITY	O-OR	D-PA	D-ME	J24	J34	J23	J25	J26,J35	J12	J13	J14
A	CN-BCL3	128.10	136.00	156.40	8.5	20.4	18.4	7.2	1.0	10.1	-0.0	-0.0
A	PF2-O	128.70	140.20	157.60	8.6	19.9	21.5	9.0	-0.0	9.4	1.0	9.5
A	BIS PF-O	131.50	141.50	158.20	7.9	20.9	22.3	8.8	-0.0	7.4	-0.0	7.0
A	P PH2-HCL	125.60	140.40	156.60	7.5	20.1	22.6	8.2	-0.0	8.5	13.0	4.0
A	P PH2-BCL3	120.40	143.80	158.70	7.3	20.3	23.4	9.0	-0.0	9.2	14.0	2.7
A	TRIS PO	132.60	142.40	158.50	7.2	20.8	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
A	TRIS PS	132.20	144.30	159.00	7.2	20.8	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
GH	SIF3-MEAN	125.30	143.40	159.80	6.6	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
A	CN-BF3	131.30	141.60	158.30	6.3	20.2	19.4	7.8	0.1	8.5	-0.0	-0.0
AJ	PCL2 MEAN	130.20	145.45	159.80	6.2	19.6	22.3	9.7	0.4	6.8	63.2	0.9
A	COCL	130.80	146.10	160.00	6.0	19.1	20.6	8.5	-0.0	7.6	-0.0	-0.0
A	TRIS PF2	132.40	146.00	159.40	6.0	19.7	21.9	7.5	-0.0	7.7	-0.0	10.3
J	PF2	138.70	147.40	162.10	5.9	18.6	21.6	9.9	-0.0	4.8	43.6	2.5
A	P PH2-O	128.80	147.30	160.10	5.9	20.6	23.4	9.2	-0.0	5.1	2.0	3.4
A	P PH2-S	128.10	148.60	160.10	5.8	20.8	23.4	8.7	0.6	5.9	-0.0	3.8
A	CN *	132.00	143.20	158.90	5.8	18.7	19.5	8.3	-0.0	7.9	-0.0	-0.0
AC	CF3 MEAN	140.15	147.75	160.30	5.8	20.0	20.2	8.4	-0.0	7.6	-0.0	-0.0
AJ	BISPCL MEAN	128.80	147.50	160.30	5.6	19.4	22.1	9.1	0.2	5.7	38.7	1.5
J	P CL NME2	127.60	149.60	161.10	5.4	19.8	22.2	8.7	1.2	6.1	51.0	1.7
A	PPH1-MO(CO)5	127.40	148.10	159.10	5.2	20.4	22.3	7.2	-0.0	6.6	5.0	1.3
A	PPH2-W(CO)5	124.40	149.20	159.30	5.2	20.6	23.7	9.2	-0.0	3.3	-0.0	1.3
A	PPH2)2POCL2	124.70	149.20	161.10	5.1	20.4	23.5	8.3	-0.0	6.7	-0.0	-0.0
B	PPH2-FE(CO)4	124.30	149.50	159.40	5.0	20.9	23.4	8.7	-0.0	6.8	-0.0	1.1
A	PPH2-CR(CO)5	124.10	149.50	159.50	5.0	20.8	23.7	8.9	-0.0	6.3	-0.0	0.9
B	PPH2-MO(CO)5	124.30	150.00	159.50	4.8	20.4	23.0	8.6	1.0	6.2	-0.0	0.9
A	CN-BBR3	135.40	146.90	159.20	4.6	21.0	22.6	8.0	-0.0	8.5	-0.0	-0.0
A	TRIS P *	130.60	147.70	159.80	4.5	20.5	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
B	PPH1	129.20	150.50	160.80	4.2	20.1	23.5	9.3	-0.0	4.6	31.1	1.1
A	PPH2	127.70	150.60	161.00	4.0	20.9	24.1	9.4	1.5	4.5	38.9	0.6
A	CO2H	139.20	151.60	162.10	4.0	20.1	21.5	8.6	1.2	5.1	-0.0	-0.0
J	BIS PH	128.60	150.50	160.40	3.8	19.4	20.3	7.1	2.4	6.5	12.3	1.6
A	TRISSNPN(CO)	120.50	150.40	160.90	3.4	19.5	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
J	BIS- PNME2	134.20	152.10	161.30	3.3	19.8	23.9	9.2	1.2	4.4	29.0	3.0
J	PET2	130.90	153.50	162.90	3.3	20.2	23.7	9.8	1.7	4.0	35.8	1.0
A	BIS SN PH2	119.40	149.60	159.30	3.0	19.2	24.7	10.3	-0.0	6.8	-0.0	-0.0
BJ	PME2 MEAN	132.05	154.15	162.95	2.9	19.8	23.2	9.4	1.8	3.6	30.1	1.7
A	BISSNPPHNCOS	119.40	150.70	159.70	2.8	19.4	26.3	10.6	-0.0	7.0	-0.0	-0.0
A	BISSN(MNCO5)	117.50	151.60	160.40	2.7	19.6	29.2	8.6	-0.0	7.5	-0.0	-0.0
A	SNPH3	117.90	151.20	159.90	2.6	19.2	22.6	9.8	1.1	6.9	-0.0	-0.0
A	SNPH2MNCO5	117.20	152.60	160.10	2.6	19.2	21.3	8.3	1.1	7.3	-0.0	-0.0
J	P (NME2)2	138.80	155.70	162.70	2.6	20.2	26.0	9.6	2.8	3.3	5.0	6.6
E	SFECO2 DIMER	127.00	152.50	159.30	2.4	21.2	24.1	8.2	3.6	3.6	-0.0	-0.0
J	PH2	128.70	153.70	161.60	2.3	19.4	23.2	9.4	1.5	3.6	3.9	1.3
CD	I MEAN	119.50	153.00	160.10	2.0	19.8	23.0	7.2	1.3	5.1	-0.0	-0.0
D	SN(CH3)3	123.00	153.50	161.40	1.9	19.1	26.7	12.0	1.5	6.5	-0.0	-0.0
A	H*	138.70	154.30	162.60	1.3	18.4	20.1	8.6	1.1	2.2	10.0	6.7
D	FGCH3	122.60	154.20	160.70	1.1	19.5	28.3	11.6	1.6	6.6	-0.0	-0.0
BCC	BR MEAN	133.20	155.20	161.00	1.1	19.9	21.6	6.3	1.6	5.5	-0.0	-0.0
CDF	CL MEAN	141.00	156.50	161.70	0.7	19.5	20.6	6.3	2.0	5.3	-0.0	-0.0
A	SH *	137.50	159.10	162.30	0.0	20.2	22.2	7.6	-0.0	3.0	-0.0	1.4
AC	CH3 MEAN	143.90	159.10	164.40	0.0	18.9	20.4	8.6	0.4	1.9	2.3	-0.0
E	SFECO2C5H5	132.20	159.30	164.30	0.0	21.2	25.0	8.2	1.4	1.4	-0.0	-0.0
A	CSIPH3	156.20	166.50	165.00	-4.3	21.6	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
A	OSIME3	158.70	167.60	165.10	-4.4	21.0	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
A	CGEPH3	157.00	169.20	166.30	-5.0	21.6	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
D	CH	164.40	171.20	165.80	-6.1	21.1	21.0	4.4	2.8	3.4	-0.0	-0.0
A	CSNPH3	160.40	172.80	168.30	-6.4	21.9	-0.0	-0.0	-0.0	-0.0	-0.0	-0.0
D	NHCH3	162.60	173.80	165.90	-6.9	21.6	21.1	4.5	2.3	3.9	-0.0	-0.0
A	NHSI(CH3)3	158.90	174.10	165.70	-7.0	21.4	21.5	4.6	2.7	3.3	-0.0	0.5
AC	NH2 MEAN	163.30	174.30	165.80	-7.0	20.4	20.2	5.1	2.3	4.6	-0.0	-0.0
A	CPEPH3	161.30	176.10	168.20	-8.0	22.2	25.2	6.0	-0.0	5.5	-0.0	-0.0

Figure 8: Input for statistics program.

chemical shifts followed by nine coupling constants. The control card selected the variables Y, X1, X2 from the input data. If a predetermined K was to be used, this was also defined on the control card. If this was left blank, the program would find the best K between two limits set in the control card (usually -10 to + 10). The program searched for the best K by trying 10 values of K between the set limits, finding the best value (lowest criterion of fit), setting new limits on either side of the best value, searching again in smaller increments of K, finding the best value of K, etc. The control card also defined the number of searches to be carried out, usually 10.

Once the best value had been found in this way or if K had been predetermined or if only one set of X variables was used, the least mean square program took over. This was basically XLSQ2, a program written at the University of Illinois and kindly donated by Dr. J. A. Plambeck, Department of Chemistry, University of Alberta. This program was modified to include the above method of selecting the variables and also to improve the output by including new statistical criteria.

The output is shown in Figures 9-12. Important features are 1) the root mean square deviation, 2) the mean deviation, 3) the criterion of fit which was in fact

LEAST SQUARE POLYNOMIAL FIT USING LSQ1

N= 61 M= 2 N1= 0 L= 1 NLA =10 FINAL K = 0.

ERROR MATRIX

4.47610E 00 -2.92099E-02
-2.92099E-02 1.91317E-04

COEFFICIENT	ERROR
7.1978570E 01	1.4962852E 00
-4.5342367E-01	9.7823137E-03

WEIGHTED SUM OF SQUARED DEVIATIONS= 2.90106E 01

ROOT MEAN SQUARE = 6.89626E-01

MEAN DEVIATION IS 0.56683

CRITERIA OF FIT = 0.026322

WHICH MEANS APPROXIMATION TO STRAIGHT LINE WAS GOOD

FINAL EQUATION IS

$Y = -0.4534 X + 71.9786$

WHERE

VARIABLES USED

Y = 4
X1A = 2
X2A = 2

Figure 9: Output of statistics program -
calculated parameters

X	Y	EVALUATION	RESIDUAL	IDENTITY
136.0000	8.5000	10.3130	1.8130	CN-BCL3
140.2000	8.6000	8.4086	-0.1914	PF2-O
141.5000	7.9000	7.8191	-0.0809	BIS PF-O
140.4000	7.5000	8.3179	0.8179	P PH2-HCL
143.8000	7.3000	6.7762	-0.5238	P PH2-BCL3
142.4000	7.2000	7.4110	0.2110	TRIS PO
144.3000	7.2000	6.5495	-0.6505	TRIS PS
143.4000	6.6000	6.9576	0.3576	SIF3-MEAN
141.6000	6.3000	7.7738	1.4738	CN-BF3
145.4500	6.2000	6.0281	-0.1719	PCL2 MEAN
146.1000	6.0000	5.7334	-0.2666	CUCL
146.0000	6.0000	5.7787	-0.2213	TRIS PF2
147.4000	5.9000	5.1439	-0.7561	PF2
147.3000	5.9000	5.1893	-0.7107	P PH2-O
148.6000	5.8000	4.5998	-1.2002	P PH2-S
143.2000	5.8000	7.0483	1.2483	CN *
147.7500	5.8000	4.9852	-0.8148	CF3 MEAN
147.5000	5.6000	5.0986	-0.5014	BISPCCL MEAN
149.6000	5.4000	4.1464	-1.2536	P CL NME2
148.1000	5.2000	4.8265	-0.3735	PPH1-MO(CO)5
149.2000	5.2000	4.3278	-0.8722	PPH2-W(CO)5
149.2000	5.1000	4.3278	-0.7722	PPH2)2PDCL2
149.5000	5.0000	4.1917	-0.8083	PPH2-FE(CO)4
149.5000	5.0000	4.1917	-0.8083	PPH2-CR(CO)5
150.0000	4.8000	3.9650	-0.8350	PPH2-MO(CO)5
146.9000	4.6000	5.3706	0.7706	CN-BBR3
147.7000	4.5000	5.0079	0.5079	TRIS P *
150.5000	4.2000	3.7383	-0.4617	PPH1
150.6000	4.0000	3.6930	-0.3070	PPH2
151.6000	4.0000	3.2395	-0.7605	CO2H
150.5000	3.8000	3.7383	-0.0617	BIS PH
150.4000	3.4000	3.7837	0.3837	TRISSNMN(CO)
152.1000	3.3000	3.0128	-0.2872	BIS- PNME2
153.5000	3.3000	2.3780	-0.9220	PET2
149.6000	3.0000	4.1464	1.1464	BIS SN PH2
154.1500	2.9000	2.0833	-0.8167	PME2 MEAN
150.7000	2.8000	3.6476	0.8476	BISSNPHMNCOS
151.6000	2.7000	3.2395	0.5395	BISSN(MNCO5)
151.2000	2.6000	3.4209	0.8209	SNPH3
152.6000	2.6000	2.7861	0.1861	SNPH2MNCOS
155.7000	2.6000	1.3805	-1.2195	P (NME2)2
152.5000	2.4000	2.8315	0.4315	SFECO2 DIMER
153.7000	2.3000	2.2874	-0.0126	PH2
153.0000	2.0000	2.6047	0.6047	I MEAN
153.5000	1.9000	2.3780	0.4780	SN(CH3)3
154.3000	1.3000	2.0153	0.7153	H*
154.2000	1.1000	2.0606	0.9606	HGCH3
155.2000	1.1000	1.6072	0.5072	D BR MEAN
156.5000	0.7000	1.0178	0.3178	F CL MEAN
159.1000	0.0000	-0.1611	-0.1611	SH *
159.1000	0.0000	-0.1611	-0.1611	CH3 MEAN
159.3000	0.0000	-0.2518	-0.2518	SFECO2C5H5
166.5000	-4.3000	-3.5165	0.7835	OSIPH3
167.6000	-4.4000	-4.0152	0.3848	OSIME3
169.2000	-5.0000	-4.7407	0.2593	OGEPH3
171.2000	-6.1000	-5.6476	0.4524	OH
172.8000	-6.4000	-6.3730	0.0270	OSNPH3
173.8000	-6.9000	-6.8265	0.0735	NHCH3
174.1000	-7.0000	-6.9625	0.0375	NHSI(CH3)3
174.3000	-7.0000	-7.0532	-0.0532	NH2 MEAN
176.1000	-8.0000	-7.8693	0.1307	OPBPH3

Figure 10: Output of statistics program - calcd.
and observed values of Y for each X.

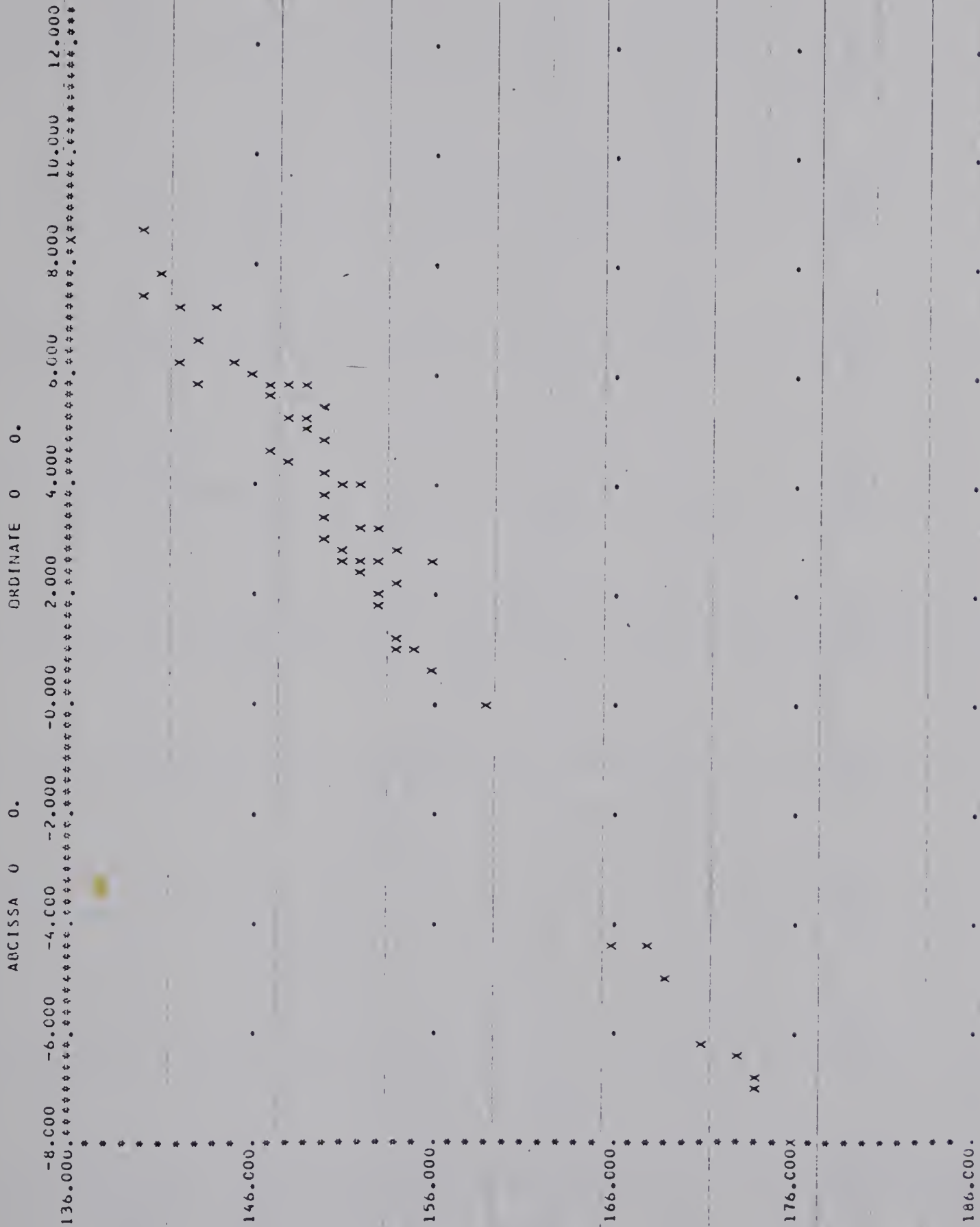


Figure 11: Output of statistics program -
Crude one page graph.

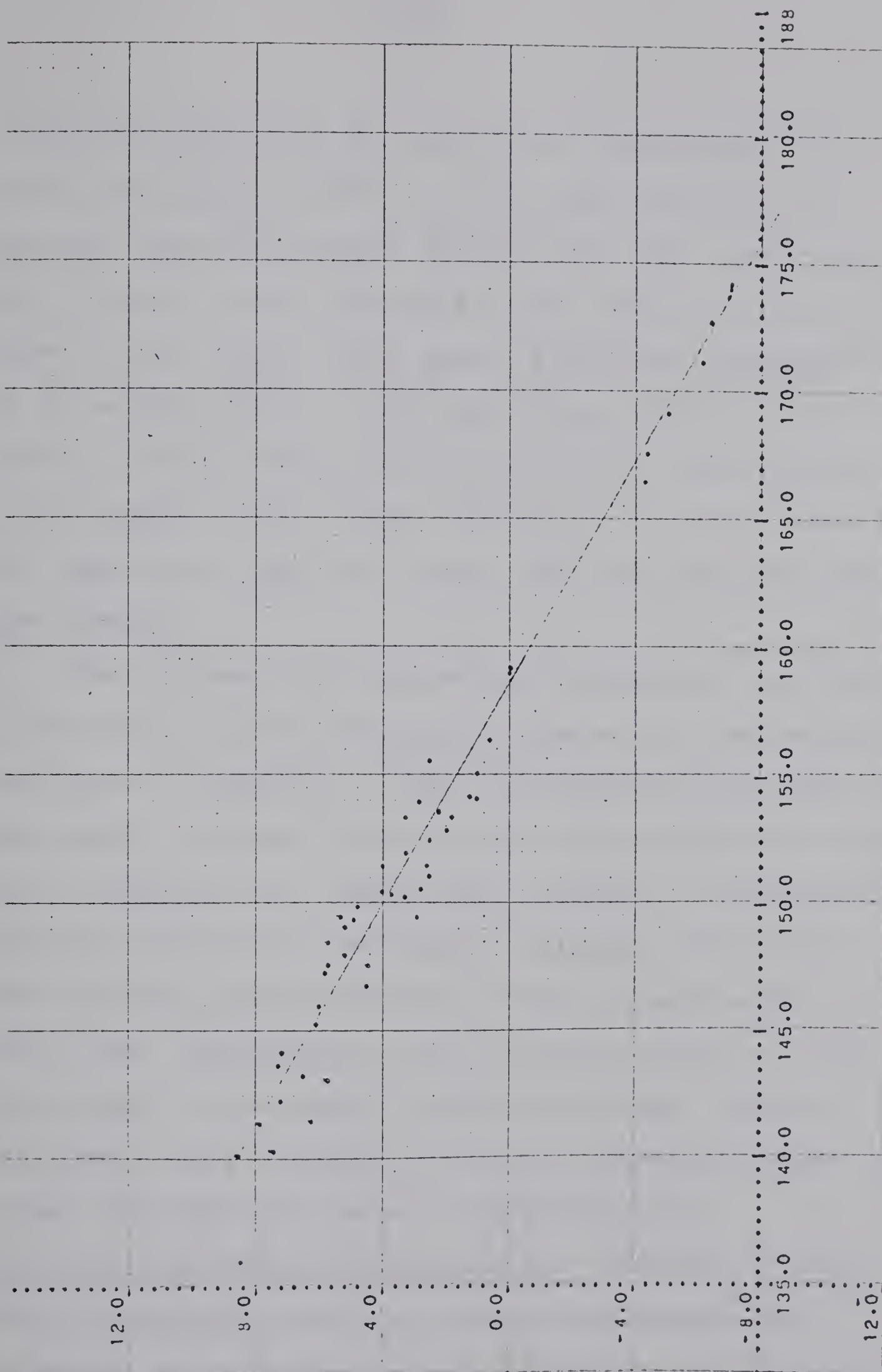


Figure 12: Output of statistics program
Graph produced by 'autoplotter'.

1 minus the square of the correlation coefficient, 4) a verbal description (G-O-F) of the approximation to a straight line which ranged through very good, good, fair, poor, bad and v.bad, depending on the value of the criterion of fit, (this was a purely subjective description by the author based on the 'look' of many plots in relation to their criteria of fit), 5) final equation and 6) the number of the column used for Y, X1 and X2 (when Y was compared to only one X value, then X1 and X2 had the same number).

Then followed the observed and calculated values of Y for each X, and the difference between the observed and calculated Y (Residual). Then followed the input data for the record. A crude one-page graph was produced for every plot. However, the program had an option in which AUTOPT could be called from the computer library. This was a data-plotting program yielding a deck of cards which if run on the "autoplotter" would plot the graph on normal graph paper to the nearest 1/50th of an inch. However, this method took an extra 20 minutes or more per graph and so was used only for the more important graphs.

The meaning of statistical parameters Before any theory can be developed to explain correlations between two variables, it is necessary to determine whether the correlation itself is valid. This somewhat obvious statement

may seem superfluous but it is surprising how misleading a semi-statistical approach can be. Examples of this occur continually in the literature leading up to this study. Usually equations were derived and only the mean deviations or possibly the root mean square deviations were given. These quantities do not describe how close the scatter of points approximates to a straight line; nor can they be used to compare correlations of different variables.

The most important criterion for the goodness of fit to a straight line is the correlation coefficient (r_{xy}) where

$$(r_{xy})^2 = \frac{(N\sum XY - \sum X \sum Y)^2}{[N\sum X^2 - (\sum X)^2][N\sum Y^2 - (\sum Y)^2]}$$

As the standard texts in statistical analysis (31,32) show, the correlation coefficient will range from unity, the value for a perfect straight line, to zero, the value if there is no correlation whatsoever.

Since we are concerned with correlations close to straight lines, it is usual to quote $(r_{xy})^2$, since the departure from unity is more noticeable.

The correlation coefficient is useful since tables are available (appendix B), whereby for a given number of points on the graph, the probability can be calculated that this correlation coefficient could have been derived

from a completely random scatter. In general, if this probability is over 5% the trend is termed not significant, if between 1% and 5%, probably significant (more experimental data required), if under 1% then the trend is highly significant. The data in Figure 14 for example shows a very highly significant trend.

Another important result derived from the correlation coefficient is that $(r_{xy})^2$ "reflects that part of the variation in one set of measurements which can be explained by dependence on the other" - page 37, reference (31). Hence for the relationship shown in Figure 14, $(r_{xy})^2$ is equal to 0.974. and this implies statistically that 97.4% of the variation in J_{24} can be explained by a linear correlation with ϕ_p ; the remaining 2.6% must be due to other factors affecting J_{24} . It must be emphasized that this does not imply a causal relationship since both variables could be due to some other factor outside our observation. The remaining 2.6% is mainly accounted for by experimental error. An error of ± 0.1 cps in J_{24} over the range of values encountered (20 cps) accounts for 1%, while an error of ± 0.2 ppm in ϕ_p (range 40 ppm) accounts for a further 1%.

This chapter deals with the compilation of data from the nmr measurements of pentafluorophenyl compounds and their analysis. The proposal is made that the $J_{24} - \phi_p$ plot provides a useful guide to the π donor-acceptor properties of the substituent.

1. F^{19} nmr data compiled for pentafluorophenyl compounds

A summary of data on 61 C_6F_5-X compounds from this and other work (16,17,18,19,22,23,24) is presented in Tables III and IV. The spectra of 44 of these compounds were recorded in this laboratory. All correlations, statistical analysis and interpretations of the nmr data have been formulated using these 61 derivatives. An additional 12 compounds were studied after the correlations had been derived and these are presented in Chapter IV. Their J_{24} and ϕ_p values will be interpreted using the proposals formulated in Chapter III.

The results from the different sources are difficult to compare due to the different conditions under which the studies were made and the strong solvent, concentration and temperature effects found in F^{19} nmr. Ranges of up to 1 cps are found for J_{23} and J_{24} for a given substituent, though 0.2 cps is commonly given as the experimental error. Other coupling constants are smaller and 0.2 cps can be

Text contd. on p. 53..

TABLES III and IV

An introduction to the tables. Tables III and IV contain all the data which is compiled and statistically evaluated in this study

The Chemical Shifts of the ortho, para and meta fluorines are listed under ϕ_o , ϕ_p and ϕ_m respectively in ppm. The ϕ -scale used here is based on $C_6F_6 = 163.0$ ppm upfield from $CFCl_3$.

The Coupling Constants are in cps. Numbering is clockwise around the ring with the substituent at 1 and the ortho fluorines at 2 and 6 (see Figure 1). The signs are based on the result of Reference (21) in combination with results from this work. The value '0' is given for unresolved coupling constants. The resolution was generally approximately 0.3 cps. Due to experimental difficulties, the resolution limit for J_{12} was approximately 2 cps.

The symbol '.....' means that analysis was not attempted. This is generally found for coupling constants derived from the meta spectrum which was sometimes broadened (e.g. for compounds with two or three pentafluorophenyl groups, spectra were usually broadened, probably by inter-ring coupling.)

The couplings to substituent atoms are arranged under columns J_{12} , J_{13} , J_{14} . For phosphines, this denotes coupling to phosphorus. For other compounds the coupling occurs to the atoms attached to the nucleus (e.g. for $C_6F_5CH_3$, position 1 denotes the methyl hydrogens).

Blanks in the table imply that the substituent atom does not possess a magnetic moment.

Sources. The data has been compiled from the following sources: A, this work HA mode; B, this work (HR mode); C, Reference (16); D, Reference (15); E, Reference (33); F, Reference (19); G, Reference (34); H, Reference (18); J, Reference (22).

TABLE III

F^{19} Chemical Shifts and Coupling Constants

J_{24}, J_{34} of Pentafluorophenyl Compounds

	ϕ_o	ϕ_p	ϕ_m	$\pm J_{24}$	$\mp J_{34}$	Ref.
C_6F_5 CNBCl ₃	128.1	136.0	156.4	8.5	20.4	A
C_6F_5 POF ₂	128.7	140.2	157.6	8.6	19.9	A
$(C_6F_5)_2$ POF	131.5	141.5	158.2	7.9	20.9	A
C_6F_5 P(C ₆ H ₅) ₂ HCl	125.6	140.4	156.6	7.5	20.1	A
C_6F_5 P(C ₆ H ₅) ₂ BCl ₃	120.4	143.8	158.7	7.3	20.3	A
$(C_6F_5)_3$ PO	132.6	142.4	158.5	7.2	20.8	A
C_6F_5 PS	132.2	144.3	159.0	7.2	20.8	A
C_6F_5 SiF ₃	143.0	6.5	G
C_6F_5 SiF ₃	125.3	143.8	159.8	6.6	H
C_6F_5 SiF ₃ Mean	125.3	143.4	159.8	6.6	GH
C_6F_5 CNBF ₃	131.3	141.6	158.3	6.3	20.2	A
C_6F_5 PCl ₂	129.5	145.8	160.2	6.2	19.7	A
C_6F_5 PCl ₂	130.9	145.1	159.4	6.2	19.4	J
C_6F_5 PCl ₂ Mean	130.2	145.4	159.8	6.2	19.6	AJ
C_6F_5 COCl	130.8	146.1	160.0	6.0	19.1	A
$(C_6F_5)_3$ PF ₂	132.4	146.0	159.4	6.0	19.7	A
C_6F_5 PF ₂	138.7	147.4	162.1	5.9	18.6	J
C_6F_5 PO(C ₆ H ₅) ₂	128.8	147.3	160.1	5.9	20.6	A
C_6F_5 PS(C ₆ H ₅) ₂	128.1	148.6	160.1	5.8	20.8	A
C_6F_5 CN	132.0	143.2	158.9	5.8	18.7	A
C_6F_5 CN	132.5	143.5	159.2	5.9	19.0	C
C_6F_5 CN Mean	132.2	143.4	159.0	5.8	18.8	AC

TABLE III

	ϕ_O	ϕ_P	ϕ_m	$\pm J_{24}$	$\mp J_{34}$	Ref
C_6F_5 CF_3	140.3	147.6	160.0	5.8	21.0	A
C_6F_5 CF_3	140.0	147.9	160.6	5.7	18.9	C
C_6F_5 CF_3 Mean	140.2	147.8	160.3	5.8	20.0	AC
$(C_6F_5)_2PCl$	128.1	147.6	160.5	5.6	19.2	A
$(C_6F_5)_2PCl$	129.5	147.4	160.1	5.5	19.6	J
$(C_6F_5)_2PCl$ Mean	128.8	147.5	160.3	5.6	19.4	AJ
C_6F_5 $PClN(CH_3)_2$	127.6	149.6	161.1	5.4	19.8	J
C_6F_5 $P(C_6H_5)Mo(CO)_5$	127.4	148.1	159.1	5.2	20.4	A
C_6F_5 $P(C_6H_5)_2W(CO)_5$	124.4	149.2	159.3	5.2	20.6	A
$[C_6F_5P(C_6H_5)_2]_2PdCl_2$	124.7	149.2	161.1	5.1	20.4	A
C_6F_5 $P(C_6H_5)_2Fe(CO)_4$	124.3	149.5	159.4	5.0	20.9	B
C_6F_5 $P(C_6H_5)_2Cr(CO)_5$	124.1	149.5	159.5	5.0	20.8	A
C_6F_5 $P(C_6H_5)_2Mo(CO)_5$	124.3	150.0	159.5	4.8	20.4	B
C_6F_5 $CNBBBr_3$	135.4	146.9	159.2	4.6	21.0	A
$(C_6F_5)_3P$	130.6	147.7	159.8	4.5	20.5	A
$(C_6F_5)_2PC_6H_5$	129.2	150.5	160.8	4.2	20.1	B
C_6F_5 CO_2H	139.2	151.6	162.1	4.0	20.1	A
C_6F_5 $P(C_6H_5)_2$	127.7	150.6	161.0	4.0	20.9	A
$(C_6F_5)_2PH$	128.6	150.5	160.4	3.8	19.4	J
$(C_6F_5)_3SnMn(CO)_5$	120.5	150.4	160.9	3.4	19.5	A
$(C_6F_5)_2PN(CH_3)_2$	134.2	152.1	161.3	3.3	19.8	J
C_6F_5 $P(CH_2CH_3)_2$	130.9	153.5	162.9	3.3	20.2	J
$(C_6F_5)_2Sn(C_6H_5)_2$	119.4	149.6	159.3	3.0	19.2	A
C_6F_5 $P(CH_3)_2$	132.1	153.9	163.0	3.0	19.7	B

TABLE III

		ϕ_o	ϕ_p	ϕ_m	$\pm J_{24}$	$\mp J_{34}$	Ref.
C_6F_5	$P(CH_3)_2$	132.0	154.4	162.9	2.8	19.8	J
C_6F_5	$P(CH_3)_2$ Mean	132.0	154.2	163.0	2.9	19.8	BJ
$(C_6F_5)_2$	$Sn(C_6H_5)Mn(CO)_5$	119.4	150.7	159.7	2.8	19.4	A
$(C_6F_5)_2$	$Sn[Mn(CO)_5]_2$	117.5	151.6	160.4	2.7	19.6	A
C_6F_5	$Sn(C_6H_5)_3$	117.9	151.2	159.9	2.6	19.2	A
C_6F_5	$Sn(C_6H_5)_2Mn(CO)_5$	117.2	152.6	160.1	2.6	19.2	A
C_6F_5	$P[N(CH_3)]_2$	138.8	155.7	162.7	2.6	20.2	J
$[C_6F_5]$	$SFe(CO)_3]_2$	127.0	152.5	159.8	2.4	21.2	E
C_6F_5	PH_2	218.7	153.7	161.6	2.3	19.4	J
C_6F_5	I	119.3	152.8	159.9	2.1	19.8	C
C_6F_5	I	119.7	153.2	150.3	1.9	19.8	D
C_6F_5	I Mean	119.5	153.0	160.1	2.0	19.8	CD
C_6F_5	$Sn(CH_3)_3$	123.0	153.5	161.4	1.9	19.1	D
C_6F_5	H	138.7	154.3	162.6	1.3	18.4	A
C_6F_5	H	139.1	154.0	162.6	1.3	18.8	C
C_6F_5	H	139.6	154.2	162.8	1.3	18.7	D
C_6F_5	H Mean	139.0	154.2	162.6	1.3	18.6	ACD
C_6F_5	$HgCH_3$	122.6	154.2	160.7	1.1	19.5	D
C_6F_5	Br	133.1	155.2	160.9	1.1	20.6	B
C_6F_5	Br	132.7	154.9	160.9	1.1	19.3	C
C_6F_5	Br	133.7	155.4	161.3	1.1	19.9	D
C_6F_5	Br Mean	133.2	155.2	161.0	1.1	19.9	BCD
C_6F_5	Cl	140.9	156.3	161.6	1.0	19.5	C
C_6F_5	Cl	141.3	156.8	161.9	0	19.5	D

TABLE III

			ϕ_o	ϕ_p	ϕ_m	$\pm J_{24}$	$\mp J_{34}$	Ref.
C_6F_5	Cl		140.8	156.3	161.5	1.0	19.6	F
C_6F_5	Cl	Mean	141.0	156.5	161.7	0.7	19.5	CDF
C_6F_5	SH		137.5	159.1	162.3	0	20.2	A
C_6F_5	CH ₃		143.7	158.8	164.6	0	19.0	A
C_6F_5	CH ₃		144.0	159.3	164.3	0	18.9	C
C_6F_5	CH ₃	Mean	143.9	159.1	164.4	0	18.9	AC
C_6F_5	SFe(CO) ₂ (C ₅ H ₅)		132.2	159.3	164.3	0	21.2	E
C_6F_5	OSi(C ₆ H ₅) ₃		156.2	156.5	165.0	-4.3	21.6	A
C_6F_5	OSi(CH ₃) ₃		158.7	167.6	165.1	-4.4	21.0	A
C_6F_5	OGe(C ₆ H ₅) ₃		157.0	169.2	166.3	-5.0	21.6	A
C_6F_5	OH		164.4	171.2	165.8	-6.1	21.1	D
C_6F_5	OSn(C ₆ H ₅) ₃		160.4	172.8	168.8	-6.4	21.9	A
C_6F_5	NHCH ₃		162.6	173.8	165.9	-6.9	21.6	B
C_6F_5	NHSi(CH ₃) ₃		158.9	174.1	165.7	-7.0	21.4	A
C_6F_5	NH ₂		163.1	174.4	165.9	-7.0	20.1	A
C_6F_5	NH ₂		163.6	174.1	165.7	-6.9	20.8	C
C_6F_5	NH ₂	Mean	163.3	174.3	165.8	-7.0	20.4	AC
C_6F_5	OPb(C ₆ H ₅) ₃		161.3	176.1	168.2	-8.0	22.2	A

TABLE IV

F^{19} Coupling Constants of Pentafluorophenyl Compounds

		\bar{J}_{23}	$\pm J_{25}$	J_{35}	$\pm J_{26}$	J_{12}	J_{13}	J_{14}	Ref.
C_6F_5	$CNBCl_3$	18.4	7.2	1.0	10.1				A
C_6F_5	POF_2	21.5	9.0	0	9.4	1.0	9.5	3.5	A
$(C_6F_5)_2$	POF	22.3	8.8	0	7.4	...	7.0	3.0	A
C_6F_5	$P(C_6H_5)_2HCL$	22.6	8.2	0	8.5	13.0	4.0	2.7	A
C_6F_5	$P(C_6H_5)_2BCl_3$	23.4	9.0	0	9.2	14.0	2.7	3.1	A
$(C_6F_5)_3$	PO	3.0	A
C_6F_5	PS	3.2	A
C_6F_5	$CNBF_3$	19.4	7.8	0.1	8.5				A
C_6F_5	PCl_2	1.0	1.1	A
C_6F_5	PCl_2	22.3	9.7	0.4	6.8	63.2	0.8	1.0	J
C_6F_5	PCl_2 Mean	22.3	9.7	0.4	6.8	63.2	0.9	1.1	AJ
C_6F_5	$COCl$	20.6	8.5	0	7.6				A
$(C_6F_5)_3$	PF_2	21.9	7.5	0	7.7	10.3	3.6	A
C_6F_5	PF_2	21.6	9.9	0	4.8	43.6	2.5	2.1	J
C_6F_5	$PO(C_6H_5)_2$	23.4	9.2	0	5.1	2.	3.4	2.3	A
C_6F_5	$PS(C_6H_5)_2$	23.4	8.7	0.6	5.9	0	3.8	3.0	A
C_6F_5	CN	19.5	8.3	0	7.9				A
C_6F_5	CN	19.9	8.2	0	7.8				C
C_6F_5	CN Mean	19.7	8.2	0	7.8				AC
C_6F_5	CF_3	21.8	8.0	0	7.6	22.2	0	1.4	A
C_6F_5	CF_3	20.2	8.4	0	7.6	1.4	C
C_6F_5	CF_3 Mean	21.0	8.2	0	7.6	22.2	0	1.4	AC
$(C_6F_5)_2$	PCl	21.5	8.9	0	5.9	37.2	1.5	1.9	A
$(C_6F_5)_2$	PCl	22.7	9.3	0.2	5.5	40.1	1.6	1.6	J

TABLE IV contd.

	\bar{J}_{23}	$\pm J_{25}$	J_{35}	$\pm J_{26}$	J_{12}	J_{13}	J_{14}	Ref
$(C_6F_5)_2PCl$ Mean	22.1	9.1	0.1	5.7	38.7	1.5	1.8	AJ
$C_6F_5PClN(CH_3)_2$	22.2	8.7	1.2	6.1	51.0	1.7	1.3	J
$C_6F_5P(C_6H_5)Mo(CO)_5$	22.3	7.2	0	6.6	5.	1.3	1.4	A
$C_6F_5P(C_6H_5)_2W(CO)_5$	23.7	9.2	0	3.3	0	1.3	1.9	A
$[C_6F_5P(C_6H_5)_2]_2PdCl_2$	23.5	8.3	0	6.7	...	0	0	A
$C_6F_5P(C_6H_5)_2Fe(CO)_4$	23.4	8.7	0	6.8	0	1.1	1.8	B
$C_6F_5P(C_6H_5)_2Cr(CO)_5$	23.7	8.9	0	6.3	0	0.9	1.7	A
$C_6F_5P(C_6H_5)_2Mo(CO)_5$	23.0	8.6	1.0	6.2	0	0.9	1.6	B
$C_6F_5CNBBBr_3$	22.6	8.0	0	8.5				A
$(C_6F_5)_2PC_6H_5$	23.5	9.3	0	4.6	31.1	1.1	0	B
$C_6F_5CO_2H$	21.5	8.6	1.2	5.1				A
$C_6F_5P(C_6H_5)_2$	24.1	9.4	1.5	4.5	38.9	0.6	0.6	A
$(C_6F_5)_2PH$	20.3	7.1	2.4	6.5	12.3	1.6	0	J
$(C_6F_5)_2PN(CH_3)_2$	23.9	9.2	1.2	4.4	29.	3.0	1.7	J
$C_6F_5P(CH_2CH_3)_2$	23.7	9.8	1.7	4.0	35.8	1.0	0.8	J
$(C_6F_5)_2Sn(C_6H_5)_2$	24.7	10.3	0	6.8				A
$C_6F_5P(CH_3)_2$	23.2	9.4	1.8	3.6	30.1	1.7	0	J
$(C_6F_5)_2Sn(C_6H_5)Mn(CO)_5$	26.3	10.6	0	7.0				A
$(C_6F_5)_2Sn[Mn(CO)_5]_2$	29.2	8.6	0	7.6				A
$C_6F_5Sn(C_6H_5)_3$	22.6	9.8	1.1	6.9				A
$C_6F_5Sn(C_6H_5)_2Mn(CO)_5$	21.3	8.3	1.1	7.3				A
$C_6F_5P[N(CH_3)]_2$	26.0	9.6	2.8	3.3	5.	6.6	2.6	J
$[C_6F_5SFe(CO)_3]_2$	24.1	8.2	3.6	3.6				E
$C_6F_5PH_2$	23.2	9.4	1.5	3.6	3.9	1.3	0	J

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TABLE IV contd.

		\bar{J}_{23}	$\pm J_{25}$	J_{35}	$\pm J_{26}$	J_{12}	J_{13}	J_{14}	Ref.
C_6F_5	I	22.9	7.3	1.4	5.2				C
C_6F_5	I	23.0	7.1	1.2	5.0				D
C_6F_5	I Mean	23.0	7.2	1.3	5.1				CD
C_6F_5	$Sn(CH_3)_3$	26.7	12.0	1.5	6.5				D
C_6F_5	H	20.1	8.6	1.1	2.2	10.0	6.7	2.5	A
C_6F_5	H	20.6	8.8	1.2	2.4	10.2	6.9	2.7	C
C_6F_5	H	21.0	8.9	1.2	2.2				B
C_6F_5	H Mean	20.6	8.8	1.2	2.2	10.1	6.8	2.6	ACD
C_6F_5	$HgCH_3$	28.3	11.6	1.6	6.6				D
C_6F_5	Br	22.1	6.1	1.2	5.5				B
C_6F_5	Br	21.0	6.3	1.8	5.6				C
C_6F_5	Br	21.8	6.4	1.7	5.4				D
C_6F_5	Br Mean	21.6	6.3	1.6	5.5				BCD
C_6F_5	Cl	20.8	6.3	2.0	5.4				C
C_6F_5	Cl	20.4	6.1	2.0	5.2				D
C_6F_5	Cl	20.7	6.4	2.0	5.3				F
C_6F_5	Cl Mean	20.6	6.3	2.0	5.3				CDF
C_6F_5	SH	22.2	7.6	0	3.0	1.4	0	A
C_6F_5	CH_3	20.5	8.8	0.2	2.0	2.3	0	1.3	A
C_6F_5	CH_3	20.3	8.5	0.6	1.8	2.3	0	1.4	C
C_6F_5	CH_3 Mean	20.4	8.6	0.4	1.9	2.3	0	1.4	AC
C_6F_5	$SFe(CO)_2(C_5H_5)$	25.0	8.2	1.4	1.4				E
C_6F_5	OH	21.0	4.4	2.8	-3.4				D
C_6F_5	$NHCH_3$	21.1	4.5	2.3	-3.9				B

TABLE IV contd.

		\bar{J}_{23}	$\pm J_{25}$	J_{35}	$\pm J_{26}$	J_{12}	J_{13}	J_{14}	Ref
C_6F_5	$NHSi(CH_3)_3$	21.5	4.6	2.7	-3.3	0.5	0.4	A
C_6F_5	NH_2	20.0	5.3	2.1	-4.6				A
C_6F_5	NH_2	20.4	4.9	2.6	-4.6				C
C_6F_5	NH_2 Mean	20.2	5.1	2.3	-4.6				AC
C_6F_5	$OPb(C_6H_5)_3$	25.2	6.0	0	-5.5				A

considered a reasonable error. Chemical shifts, being more sensitive to differences in solvent and concentration, show greater variations. Values differing by as much as 2 ppm are reported for the chemical shift of a given fluorine. Our brief study of concentration effects has shown that corrections are difficult to apply, since, upon dilution, chemical shifts are changed both upfield and downfield and to different extents. Upon dilution from ca. 20 mole % to 5 mole % in benzene, the following changes in the chemical shift of the para-fluorine were found: $C_6F_5P(C_6H_5)_2$, 0.2 ppm downfield; C_6F_5CN , 0.8 ppm upfield; $(C_6F_5)_2PCl$, 1.0 ppm downfield; $(C_6F_5)_3P$ and C_6F_5H , no change. Variations in the reported chemical shifts for the same compound can also be found due to the choice of the standard. Although F^{19} chemical shifts have commonly been measured by using trichlorofluoromethane as reference and solvent, hexafluorobenzene has been found to be a better reference and benzene a more suitable solvent. A recent quantitative approach to solvent effects on fluorine chemical shifts (27) supports this and shows that if $CFCl_3$ is used as a universal reference, measured chemical shifts may differ by 2-3 ppm depending upon choice of solvent. However, if $CFCl_3$ is used for aliphatic compounds and C_6F_6 for aromatic compounds, errors up to 0.5 ppm can be expected. We have found these uncertainties to be of the same magnitude as the differences

found in Table III. Hexafluorobenzene has six times as many fluorines giving a single sharp peak. Less reference need be used, which permits the use of more suitable solvents and gives a better approximation to the infinite dilution ideal. The chemical shift of hexafluorobenzene relative to trichlorofluoromethane has been reported at values ranging from 162.23 ppm (15) to 163.9 ppm (17). In this work, concentrations in the range 20 - 30% w/w or v/v (approximating 10 mole %) were used, this being effectively the lowest concentration at which both chemical shifts and coupling constants could be conveniently measured. The value 163.0 is used for conversion to the CFCl_3 scale. Under similar conditions, other workers (16) have found 162.9 ppm. These variations show that at this early stage in the development of fluorine nmr, standardization in measuring and reporting chemical shifts has yet to become effective. Hence in order to compare our work with other data from the literature, the other results are adapted to correspond as closely as possible to our choice of conditions.

For purposes of comparison, the data taken from the sources mentioned in Tables III and IV were adjusted in two cases. N. Boden et al., (15) in measurements of chemical shifts at infinite dilution found C_6F_6 to be 162.23 ppm from CFCl_3 . Chemical shifts were measured relative to

C_6F_6 but quoted relative to $CFCl_3$ by adding 162.23 ppm. To bring these into line with the scale $C_6F_6 = 163.0$, 0.77 ppm was added to each shift. M. G. Barlow et al. (22) measured chemical shifts in 50% solutions. Comparing the four compounds of their work that were also analyzed in this work, it was found that the chemical shifts averaged 1.4 ppm higher. This discrepancy, which was no doubt due to concentration effects, was accounted for by subtracting 1.4 ppm from all chemical shifts from that source. Although it is realized that solvent effects change the chemical shifts of the ortho, para and meta fluorines in different ways, there seems no other way of accomodating all results measured under different conditions than by the gross assumptions outlined above. Coupling constants, being less sensitive to concentration changes, were not adjusted for differences in the conditions of measurement. In the statistical analysis, the mean values of chemical shifts and coupling constants were used when quoted from more than one source.

A close examination of the results in Table III shows that ortho-fluorine chemical shifts (ϕ_o) fall in the range 117-164 ppm., meta-fluorine chemical shifts (ϕ_m) in the range 156-169 ppm and para chemical shifts (ϕ_p) in the range 136-176 ppm. These changes can be seen in Figure 13 as illustrated by 12 common organic substituents. The re-

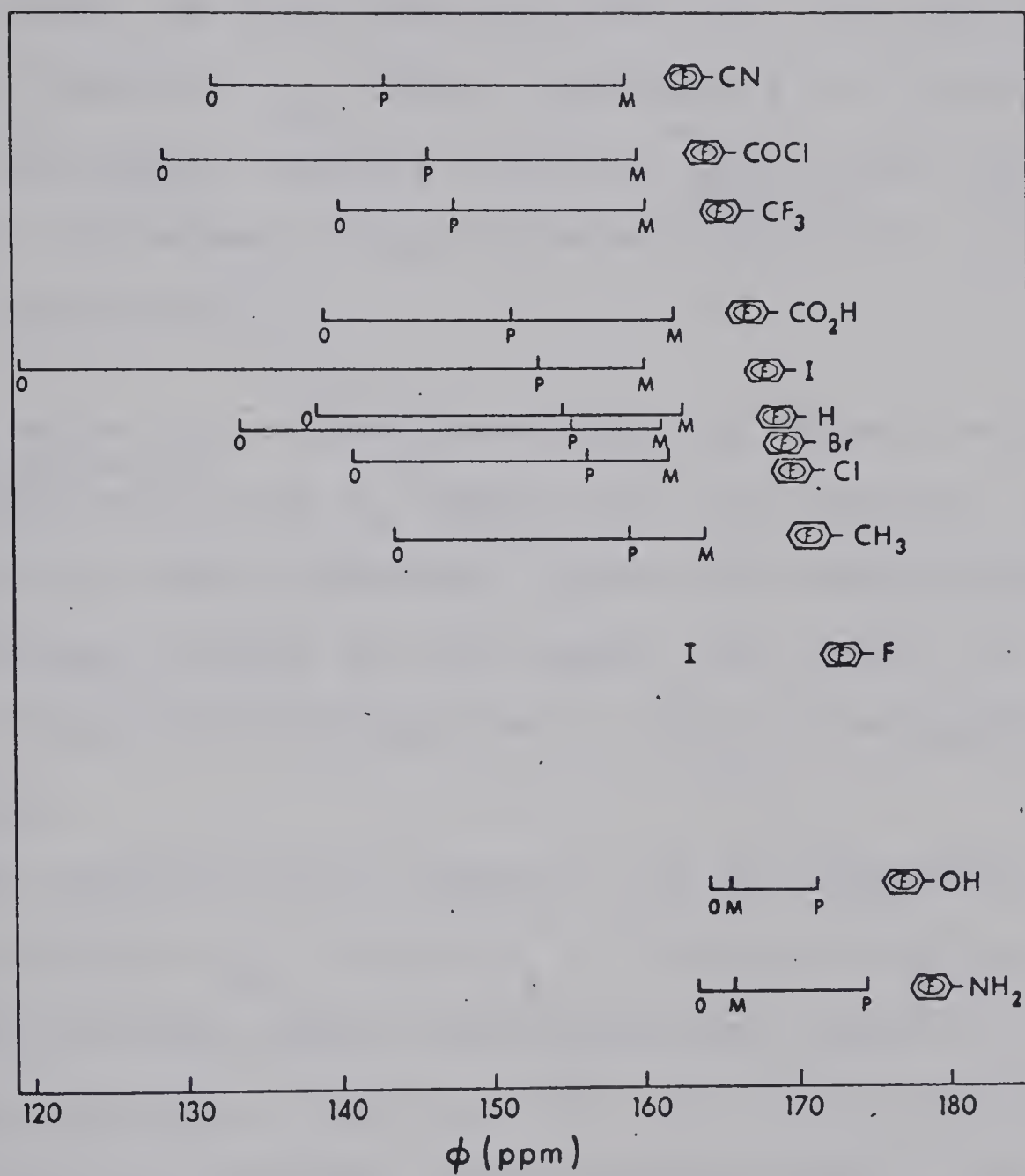


Figure 13. The chemical shifts of the ortho, para and meta fluorines for the common organic substituents.

sults in Tables III & IV show that the ortho coupling constants, J_{23} and J_{34} , varied little with substituent. The mean value for J_{23} was 22.7 cps. The mean value for J_{34} was 20.9 cps. No trends were discerned for the only para coupling constant, J_{25} , which ranged from 4 to 12 cps. Of the three meta coupling constants J_{24} , J_{26} and J_{35} , the first two showed obvious correlations with the nature of the substituent.

2. J_{24} versus ϕ_p . It was found that J_{24} formed a straight line relationship with ϕ_p (Figure 14) and, moreover, could be related to other parameters. Since this relationship is a principal concern of this thesis, the results of Tables III and IV are tabulated in order of decreasing J_{24} values.

The straight line in Figure 14 can be represented algebraically by $J_{24} = -0.453 \phi_p + 71.98$, as found by a computerized least square method (Equation 1 Table V.) The root mean square deviation (RMS) for a plot of all 61 substituents was 0.69 cps. The goodness of fit of the data to a straight line, as defined by the square of the correlation coefficient $(r_{xy})^2$, for the plot of 61 sub-

$$(r_{xy})^2 = \frac{(N\sum XY - \sum X \sum Y)^2}{[N\sum X^2 - (\sum X)^2][N\sum Y^2 - (\sum Y)^2]}$$

stituents was 0.974.

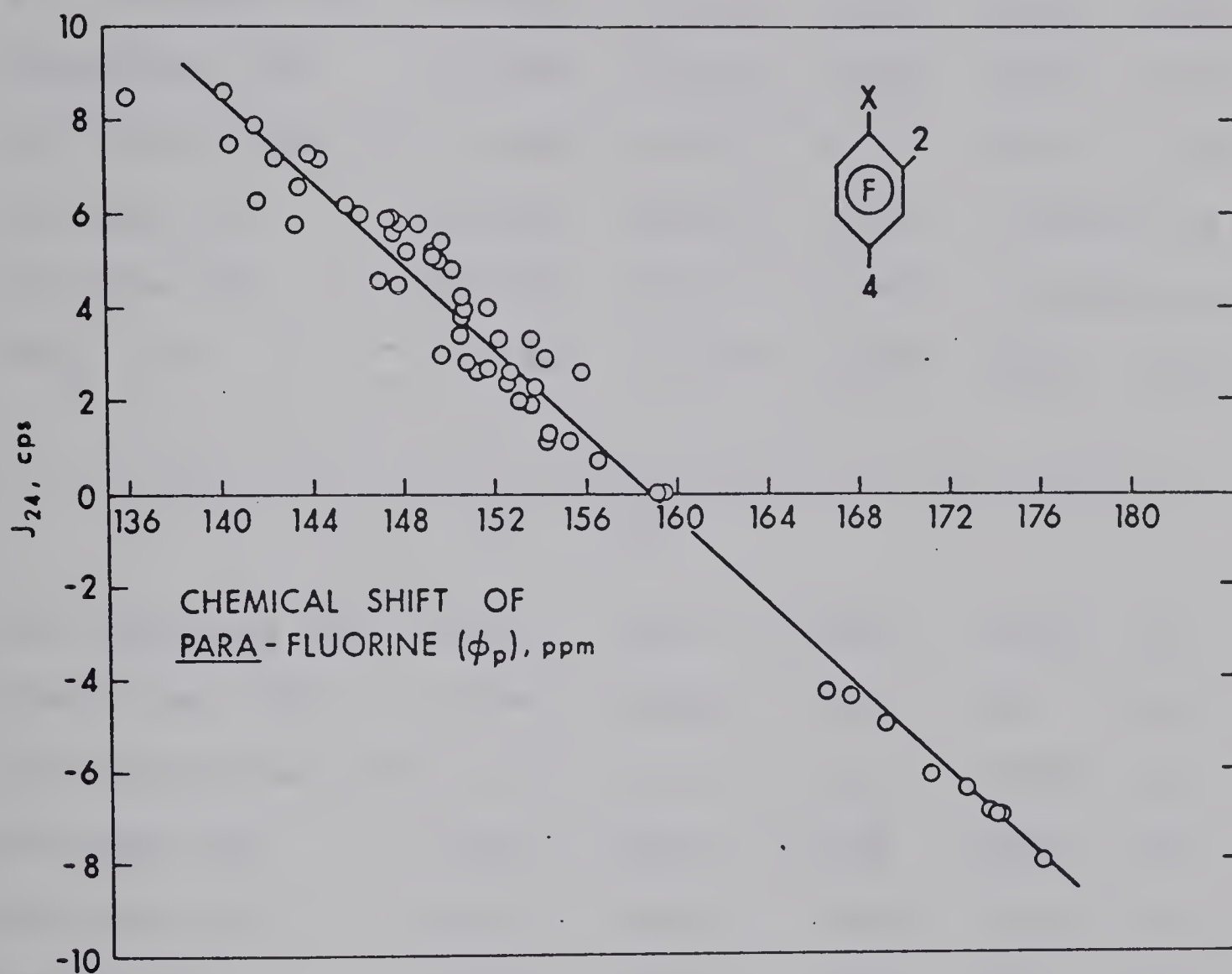


Figure 14. The relationship of the coupling constant between the ortho and para fluorines (J_{24}) to the chemical shift of the para fluorine (ϕ_p) for all 61 pentafluorophenyl derivatives.

TABLE V

Equations Relating J_{24} to the Chemical Shifts of the
Para and Meta Fluorines^a

	a	c	$(r_{xy})^2$	G-O-F	RMS
	$J_{24} = a \phi_p + c$				
1 All compounds (61)	-0.453	71.98	0.974	GOOD	0.69
2 Phosphines (28)	-0.390	62.98	0.932	GOOD	0.42
3 Tin derivatives (7)	-0.290	46.57	0.72	POOR	0.22
4 Halogens (3)	-0.375	59.41	0.995	V.GOOD	0.04
5 Nitriles (4)	-0.359	57.30	0.996	V.GOOD	0.08
6 OMR_3^b (6)	-0.396	61.89	0.984	GOOD	0.16
	$J_{24} = a \phi_m + c$				
7 All Compounds (61)	-1.47	239.3	0.84	FAIR	1.7
8 Phosphines (28)	-0.86	142.8	0.67	BAD	0.9
9 Tin derivatives (7)	-0.24	41.5	0.15	V.BAD	0.4
10 Halogens (3)	-0.82	133.4	0.98	GOOD	0.1
11 Nitriles (4)	-1.27	206.8	0.96	GOOD	0.3
12 OMR_3^b (6)	-0.72	114.2	0.66	BAD	0.7
13 All Compounds (61)	$J_{24} = 0.524\phi_p$		0.98	GOOD	0.65
	+ 0.262 ϕ_m				
	+ 40.69				

^aFigures in parenthesis refer to the number of points from which the equation is derived. RMS is the root mean square deviation; $(r_{xy})^2$ is the square of the correlation coefficient. G-O-F is the name given to the goodness of fit (p. 39)

^bPentafluorophenoxy derivatives in which M = Si, Ge, Sn, Pb and
R = C_6H_5 or CH_3

The values of $(r_{xy})^2$, which range from 0 to 1 as the completely random scatter of points approaches a perfect straight line, are reported in preference to RMS values which can give misleading results. An examination of Tables V, VI, XII, IX and X provides many examples where the root mean square for a poor straight line (i.e., one having a low $(r_{xy})^2$ value) is less than the RMS value for a good straight line. This is the result when the range of values for the poor straight line is not as great as the range of values for the good straight line. Details of the computerized statistical analysis are also found in Chapter II and Appendix A & B.

It should be noted that for the very wide range of substituents measured or plotted from data of other workers, only two points (CN-BCl₃, CN-BF₃) existed outside 2.2 standard deviations. These two points, however, formed a very good straight line when linked with the two similar substituents -CN, and -CN-BBr₃. Two other compounds (C₆F₅)₃P and (C₆F₅)₃PO, which were previously reported (35) at values inconsistent with this plot, were remeasured giving more explicable results. For plots of groups of similar substituents (results summarized in Table V) such as the phosphines, benzonitriles, halobenzenes, and the phenoxy derivatives of group IV organometallic compounds, the RMS was close to the experimental error (0.2 cps).

This is also true for the tin derivatives but in this case, the results are not so meaningful since the $(r_{xy})^2$ value was low. The spread of the tin points is not very large.

The sign change was demonstrated by comparing the sign of J_{24} relative to J_{23} for the two compounds pentafluorobenzoyl chloride and pentafluoroaniline. For pentafluorobenzoyl chloride, J_{24} and J_{23} were of opposite sign, whereas for pentafluoroaniline J_{24} was of the same sign as J_{23} . Since J_{23} remained approximately constant at 20 cps for all 61 derivatives it was assumed that J_{23} did not change sign. A detailed account of the sign determination has been given in Chapter II. These sign designations are consistent with two previous determinations. Snyder and Anderson (36) found that the J_{FF}^{meta} in hexafluorobenzene, as observed in the nematic liquid crystal, was -4 cps and therefore was of the same sign as J_{FF}^{ortho} , which was assumed to be negative. The interpolated value of J_{24} for hexafluorobenzene using figure 14 is -2.0 cps, the value of J_{24} corresponding to $\phi_p = 163.0$. It is presumed that the very different conditions of measurement have caused this discrepancy between the two results.

A recent determination of relative signs and coupling constants has been made on iodopentafluorobenzene using low field nmr (21). Basing the signs on J_{FF}^{ortho} being negative, the signs of J_{26} and J_{35} were both found to be

negative while the third meta-coupling constant, J_{24} , was found to be anomalously positive. Since our results show that the sign change of J_{24} occurs for substituents with ϕ_p above 158 ppm, the apparent inconsistency between the sign of J_{24} for iodopentafluorobenzene and hexafluorobenzene is resolved.

3. J_{24} versus ϕ_m . The weaker relationship between J_{24} and ϕ_m is shown in Table V. Since the J_{24} values are the same in relationships with ϕ_m and ϕ_p , the equations derived from the same number of points can be compared by their RMS value as well as their $(r_{xy})^2$ value. It can be seen that the RMS value of the ϕ_m series is in each case more than double that for the ϕ_p series.

The last equation in Table V shows that an even better correlation exists for the combination of ϕ_p and ϕ_m when related to J_{24} . The combination of ϕ_p and ϕ_m found to give the best straight line was $\phi_p - 0.50 \phi_m$.

4. J_{26} versus ϕ_p . In the analysis of the pentafluorophenyl group, it was noted that the pair of coupling constants, J_{26} and J_{35} , were indistinguishable. However the study of iodopentafluorobenzene mentioned above yielded the unambiguous assignment $|J_{26}| > |J_{35}|$ to which we have adhered. When J_{26} is plotted against ϕ_p , a straight line relationship is found (Figure 15a and Equation 1, Table VI). Like the J_{24} - ϕ_p plot,

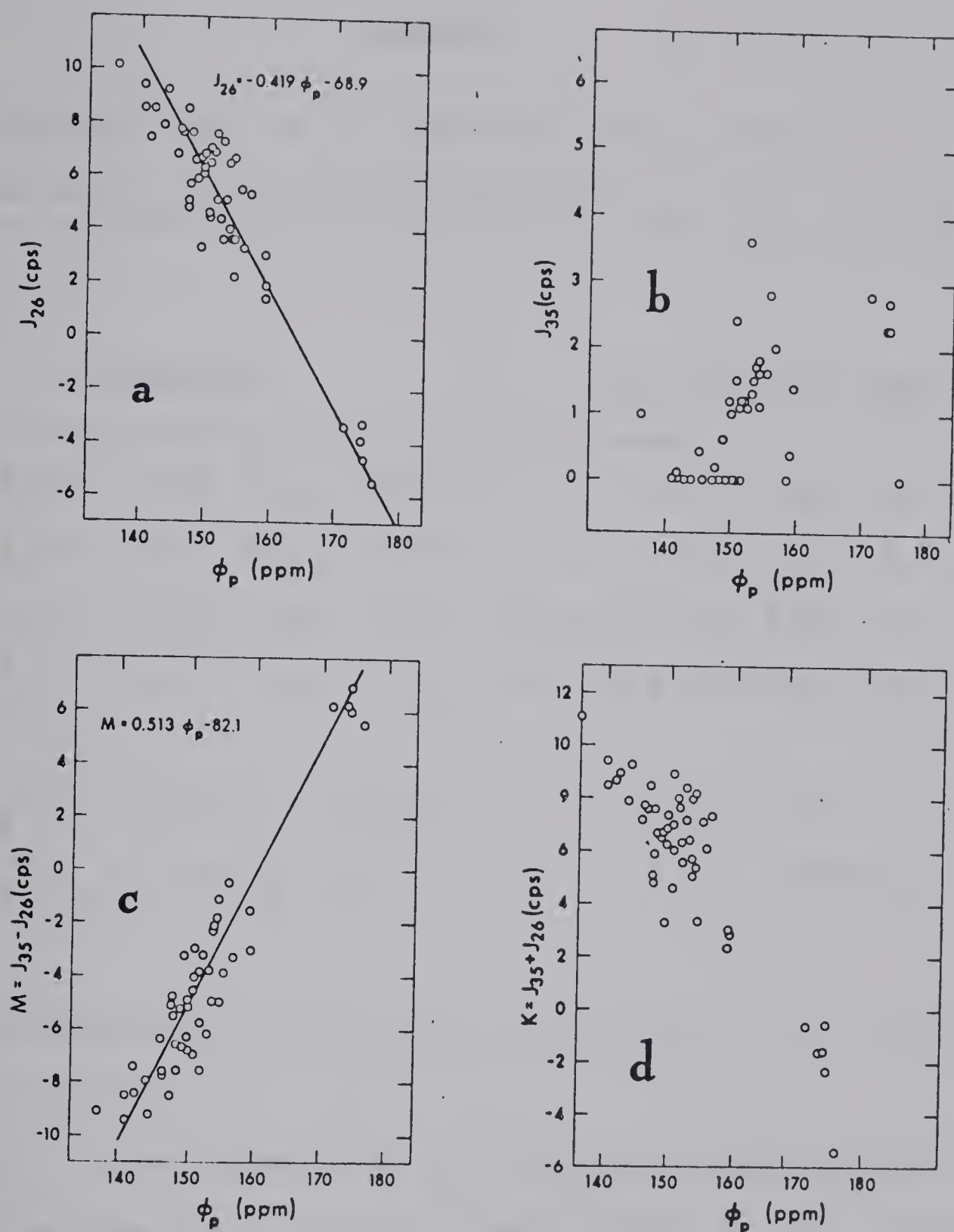


Figure 15. The relationship of the chemical shift of the para fluorine (ϕ_p) to the coupling constant between the two fluorines at the ortho positions, 2 and 6 (J_{26}), the coupling constant between the two fluorines at the meta positions, 3 and 5 (J_{35}) and the two experimentally derived parameters, $K(=J_{26} + J_{35})$ and $M(=J_{26} - J_{35})$. The absolute sign of J_{26} has now been established as the opposite of that shown in figure 5a.

TABLE V

Equations Derived by Least Mean Square Analysis,^a
Relating ϕ_p with Coupling Constants J_{26} , J_{35} , J_{13} , J_{14}

	Equation	$(r_{xy})^2$	G-O-F	RMS	Pts.
1	$\phi_p = -2.38 J_{26} + 164.19$	0.84	FAIR	3.4	61
2	$\phi_p = 5.31 J_{35} + 146.90$	0.51	BAD	6.0	61
3	$\phi_p = 1.95 (J_{35} - J_{26}) + 160.08$	0.88	FAIR	3.0	61
4	$\phi_p = 2.52 (J_{35} + J_{26}) + 167.35$	0.65	BAD	5.1	61
5	$J_{13}^b = 0.299 \phi_p + 47.38$	0.18	V.BAD	2.6	20
6	$J_{14}^c = -0.130 \phi_p + 21.40$	0.37	V.BAD	0.7	22

^a $(r_{xy})^2$ is the square of the correlation coefficient; G-O-F is the name given to the goodness of fit (p. 39); RMS is the root mean square deviation and Pts. is the number of points used in the analysis.

^b coupling constant between phosphorus and meta fluorine

^c coupling constant between phosphorus and para fluorine

the points with ϕ_p greater than 170 ppm are incorporated into the straight line relationship by means of a sign change in J_{26} for these points. Since the point corresponding to iodopentafluorobenzene lies in the main group, the absolute sign of the main group is established as negative. An absolute positive sign is therefore given to J_{26} for points with $\phi_p > 170$ ppm.

It was not possible to designate J_{35} with relative or absolute signs since its value was generally less than 3 cps, with many couplings unresolved (Figure 15b.) Thus the J_{35} values with $\phi_p < 160$ ppm could not be established as having any one sign and consequently there was no way of determining the signs of J_{35} with $\phi_p > 170$ ppm.

It was assumed in this work that for compounds with $\phi_p < 160$ ppm, $|J_{26}| > |J_{35}|$. This relationship appears to hold for $\phi_p > 170$ ppm. The opposite would have resulted in these points being above the straight line of Figure 15a. However the scatter in J_{26} does not preclude the possibilities of $|J_{26}| < |J_{35}|$ for points with $\phi_p > 170$ ppm.

Table IV and Figure 15 shows that $K(=J_{26} + J_{35})$ and $M(=J_{26} - J_{35})$, the two nmr parameters experimentally derived from AA'XX' spectra, also give straight line plots. The problem of assigning relative signs and relative magnitudes to the J_{26} , J_{35} pair for compounds with $\phi_p > 170$ ppm is due to the lack of points in the region ϕ_p between

160 and 170 ppm. This is caused only by the difficulty in analysing spectra, which is complicated in this region by the overlapping of the meta multiplet with either the para or the ortho multiplets.

As can be seen from Figure 15a and the statistical parameters in Table VI, the considerable scatter in the $J_{26} - \phi_p$ plot reduces its predictive value, in contrast to the $J_{24} - \phi_p$ plot, which is sufficiently linear to be applied in the evaluation of substituent effects.

5. Phosphorus-fluorine coupling constants. Other substituent effects on coupling constants can be found in the series of phosphines studied. The most striking change is shown in the J_{12} values (Table VII). The J_{12} values in three-coordinate phosphorus compounds fall within the range 30 - 60 cps except for the three compounds $C_6F_5PH_2$, $(C_6F_5)_2PH$ and $C_6F_5P[N(CH_3)_2]_2$, which show anomalously low values. However, a marked decrease of coupling occurs when phosphorus expands its coordination. For example, J_{12} for $C_6F_5PF_2$ drops from 44 cps to 1 cps upon oxidation to $C_6F_5POF_2$. Similarly, J_{12} in $C_6F_5P(C_6H_5)_2$ is 39 cps, but decreases to 2 cps in $C_6F_5PO(C_6H_5)_2$ and to less than 2 cps (not resolved) in $C_6F_5PS(C_6H_5)_2$ and in the metal carbonyl complexes.

The trends of other phosphorus-fluorine coupling

TABLE VII

The Phosphorus-ortho-Fluorine Coupling Constant (J_{12}) for
some Pentafluorophenylphosphine Derivatives

Mono C_6F_5 derivatives	J_{12}^a	Bis C_6F_5 derivatives	J_{12}^a
Three Coordinate Phosphorus			
$C_6F_5-PCl_2$	$63.2^{c,d}$	$(C_6F_5)_2PCl$	$38.7^{c,d}$
$C_6F_5-PCl[N(CH_3)_2]$	51.0^d		
$C_6F_5-PF_2$	43.6^d		
$C_6F_5-P(C_6H_5)_2$	38.9^c	$(C_6F_5)_2P(C_6H_5)$	31.1^c
$C_6F_5-P(CH_2CH_3)_2$	35.8^d		
$C_6F_5-P(CH_3)_2$	$30.1^{c,d}$		
$C_6F_5-P[N(\text{tert-but})_2]_2$	39.0^d		
$C_6F_5-P[N(CH_3)_2]_2$	$5.^d$	$(C_6F_5)_2PN(CH_3)_2$	29.0^d
$C_6F_5-PH_2$	3.9^d	$(C_6F_5)_2PH$	12.3^d
Four Coordinate Phosphorus			
$C_6F_5-POF_2$	1.0^c	$(C_6F_5)_2P(C_6H_5)Mo(CO)_5$	$5.^c$
$C_6F_5-P(C_6H_5)_2^0$	$2.^c$		
$C_6F_5-P(C_6H_5)_2S$	unresolved ^{b,c}		
$C_6F_5-P(C_6H_5)_2-M(CO)_X$	unresolved ^{b,c}		
M = Cr, Mo, W, Fe			
X = 5, 5, 5, 4			

a) in cps.

b) less than 2 cps.

c) This work

d) Reference (22)

constants (J_{13} and J_{14}) indicated previously by Hogben, Gay and Graham (37) have not been validated by the increased amount of data (see Equations 5 and 6, Table VI). It does appear that in general strong electron withdrawing groups give larger values for J_{13} and J_{14} , but with some exceptions.

6. ϕ_o against electronegativity of substituent atom.

Table VIII and Figure 16 show that ϕ_o , the chemical shift of the ortho-fluorine exhibits a fair relationship to the Allred-Rochow electronegativities of the substituent atom directly bonded to the pentafluorophenyl ring. Substituents of similar type, $-\text{PH}_2$, $-\text{SH}$, $-\text{CH}_3$, $-\text{NH}_2$, $-\text{OH}$ also form a reasonable straight line relationship within the overall plot. A least mean square analysis showed that ϕ_p did not contribute appreciably to the relationship (Equations 1 and 2 of Table VIII).

7. Interpretation with respect to electronic interactions

In the plot of J_{24} against ϕ_p (Figure 17) the positions of the common organic substituents reveal the presence of an empirical relationship involving the electron donor-acceptor properties of the substituents. Electron donating substituents such as $-\text{NH}_2$ and $-\text{OH}$ give high ϕ_p values with large negative J_{24} values. Substituents intermediate in electron donation or acceptance such as $-\text{H}$ and $-\text{CH}_3$ give intermediate ϕ_p values and near zero J_{24} values.

TABLE VIII

Equations Derived by Least Mean Square Analysis,^a Relating the Electronegativity,^b ϵ , of the Substituent Atom to the Chemical Shift of the ortho-fluorine, ϕ_o .

Equations	$(r_{xy})^2$	G-O-F	RMS	Pts. ^c
$\epsilon = 0.0371 \phi_o - 2.68$	0.81	Fair	0.23	75
$\epsilon = 0.0370 \phi_o + 0.0003 \phi_p - 2.70$	0.81	Fair	0.23	75

^a $(r_{xy})^2$ is the square of the correlation coefficient;
G-O-F is the name given to the goodness of fit as derived on page 39 ; RMS is the root mean square deviation and the Pts is the number of points used in the analysis.

^bElectronegativities are those of Allred and Rochow as given in reference (38).

^cThe extra 14 points are found from chemical shifts in the literature for C_6F_5X where $X = Mn(CO)_5, BCl_2, BF_2, BCl_2$ pyridine, BF_2 pyridine, $B(OH)_2, C_6F_5, B(Cl)C_6F_5, Ti(C_5H_5)_2C_6F_5, Tl(Br)C_6F_5, Hg(C_6F_5), Fe(CO)_2C_6H_5$ and NO_2 :
References (39,40,41,14).

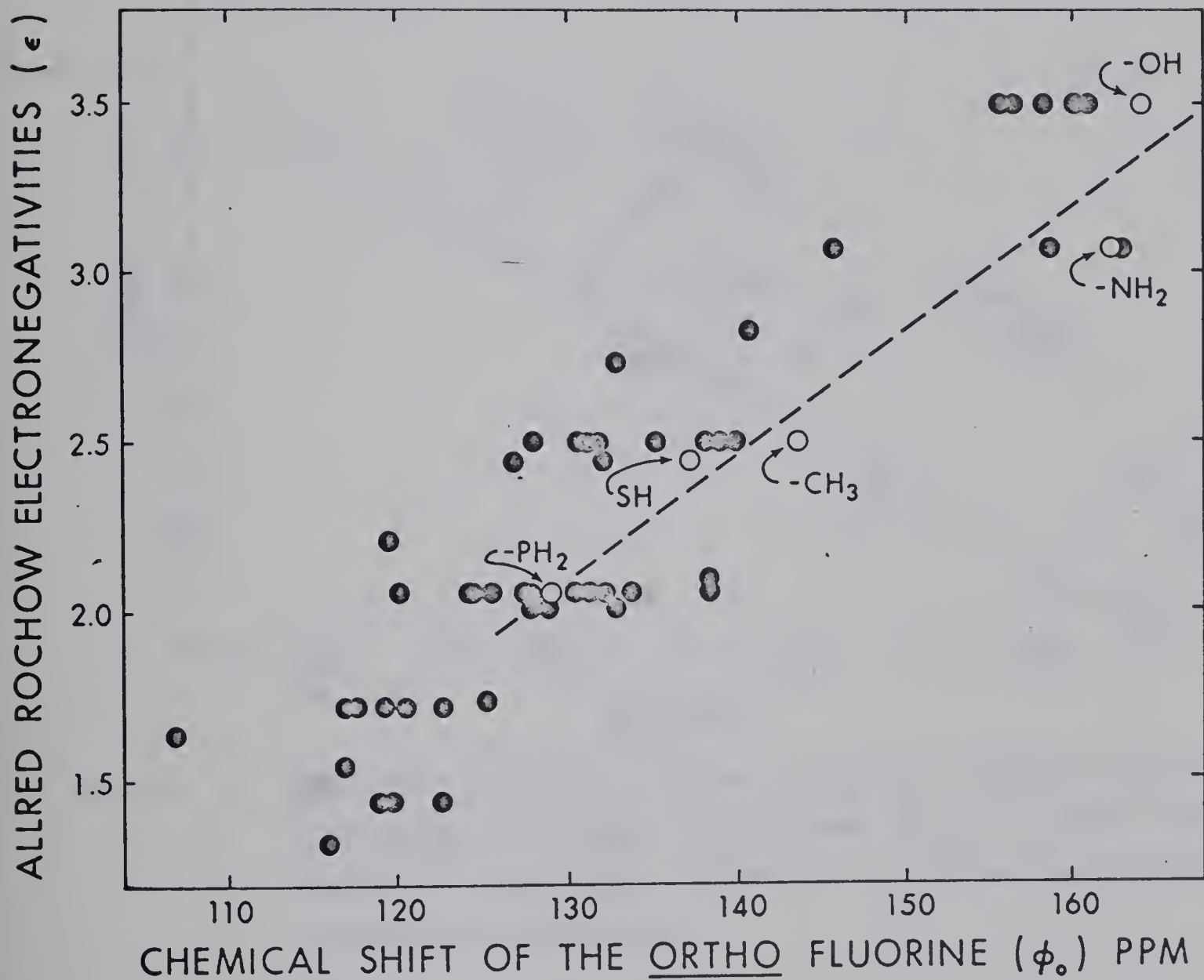


Figure 16. The relationship of the electronegativity of the substituent atom to the chemical shift of the ortho fluorine.

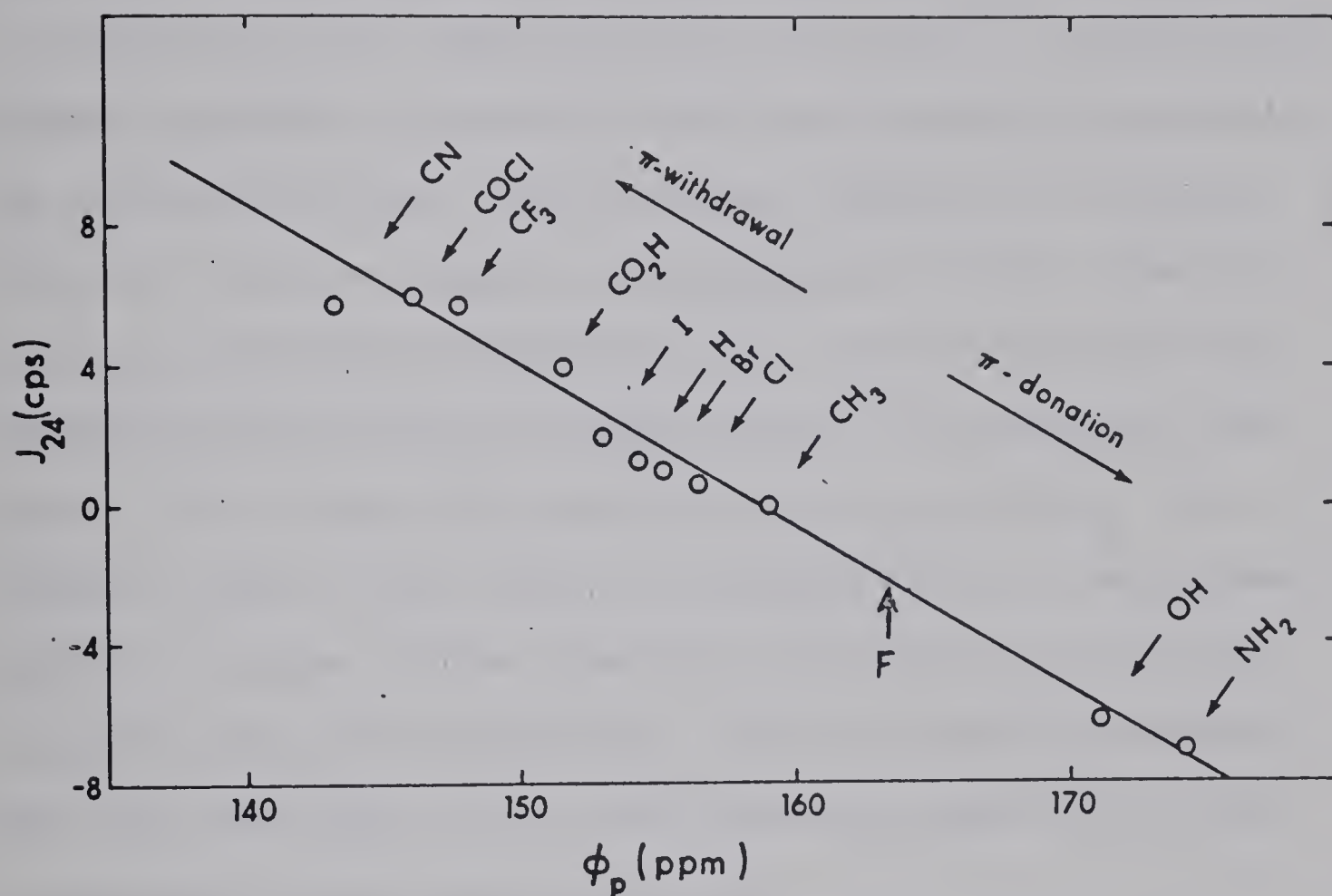


Figure 17. The relationship of the coupling constant between the ortho and para fluorines (J_{24}) to the chemical shift of the para fluorine (ϕ_p) for the common organic substituents.

Substituents that accept electrons from the benzene ring (e.g., -CN, -COCl) result in low ϕ_p values with high J_{24} values. There is theoretical support for some aspects of this essentially empirical relationship in that attempts to rationalize the chemical shifts of nuclei in substituted aromatic systems in terms of electronic interaction within the molecule have met with success. However, no correlation of fluorine coupling constants with either chemical shift or π -electron distribution in the molecule had been reported previous to the Communication of Hogben, Gay and Graham (37), where the correlation of J_{24} with ϕ_p , the change in sign of J_{24} , and an interpretation of both these effects in terms of the electronic character of the substituent group were described. Certain coupling constants have now been shown to be predictable by additivity rules in polysubstituted benzenes (42,43).

In the absence of anisotropic and paramagnetic effects, the chemical shift is understood to be a measure of the electron density as seen by the nucleus. Substituent effects on the electronic distribution can therefore be observed by the measurement of chemical shifts of nuclei at different positions in the benzene ring. The classical concept of electronic interactions predicts changes in electron density at the ortho- and para-positions when the substituent exhibits resonance effects,

whereas changes in electron density at the meta position indicate the inductive effect of the substituent. These two effects refer to the electronic interactions between the substituent and the substituted carbon and are generally considered to be π -resonance and σ -inductive. In view of the rapid diminution of inductive effects through a σ -bond framework, it seems that both inductive and resonance components initiated by the substituent must be transmitted to the meta and para positions by the π -electrons of the ring if their effects are to be experienced at these positions. This separation of the overall ring-substituent interaction into inductive and resonance effects seems the most appropriate one to be used in this study. It should be noted, however, that another school of thought defines any effect which distorts the π -system as a resonance effect (44). Introduction of the resonance effects into the benzene π -system is accomplished by simply extending the π network. However, in order that the inductive effect be transmitted via the benzene π -system, it is implicit that the substituent inductive effect along the σ -bond must somehow polarize the π electrons of the substituted carbon atom.

In a study of C^{13} and H^1 chemical shifts in monosubstituted benzenes, Spiesecke and Schneider (8) have shown that para-carbon shifts are dependent upon the change in π -electron density at the para-carbon arising from the

resonance effects of individual substituents. They also concluded that inductive and magnetic anisotropic contributions were negligible at the para carbon. Furthermore they found that para-proton shifts paralleled those of the para-carbon. The important implication was noted that the intervening σ -bond cause no extraneous effects since the magnetic field at the hydrogen nucleus still reflected the π -electron distribution at the para-carbon. Spiess and Schneider also found that inductive effects did not extend to the meta- positions in phenyl derivatives since variations in C^{13} and H^1 shifts were small, uniform and apparently unrelated to the general electronegativity of the substituent. Only in the case of the monometa-fluorophenyl series of Taft has there been found a correlation of fluorine shift with the inductive effect of the substituent exclusively (45).

Although C^{13} chemical shifts are not available for our pentafluorophenyl compounds, it is interesting to find that the para-fluorine chemical shifts form a straight line relationship with the para-carbon shifts from the corresponding phenyl derivatives as shown in Figure 18. Previous work on pentafluorophenyl derivatives has shown that the meta- and para- F^{19} shifts can be successfully predicted from the π -electron charge densities and bond orders as calculated by the Hückel molecular orbital method (5, 15, 46). Changes in the π -electron charge density result

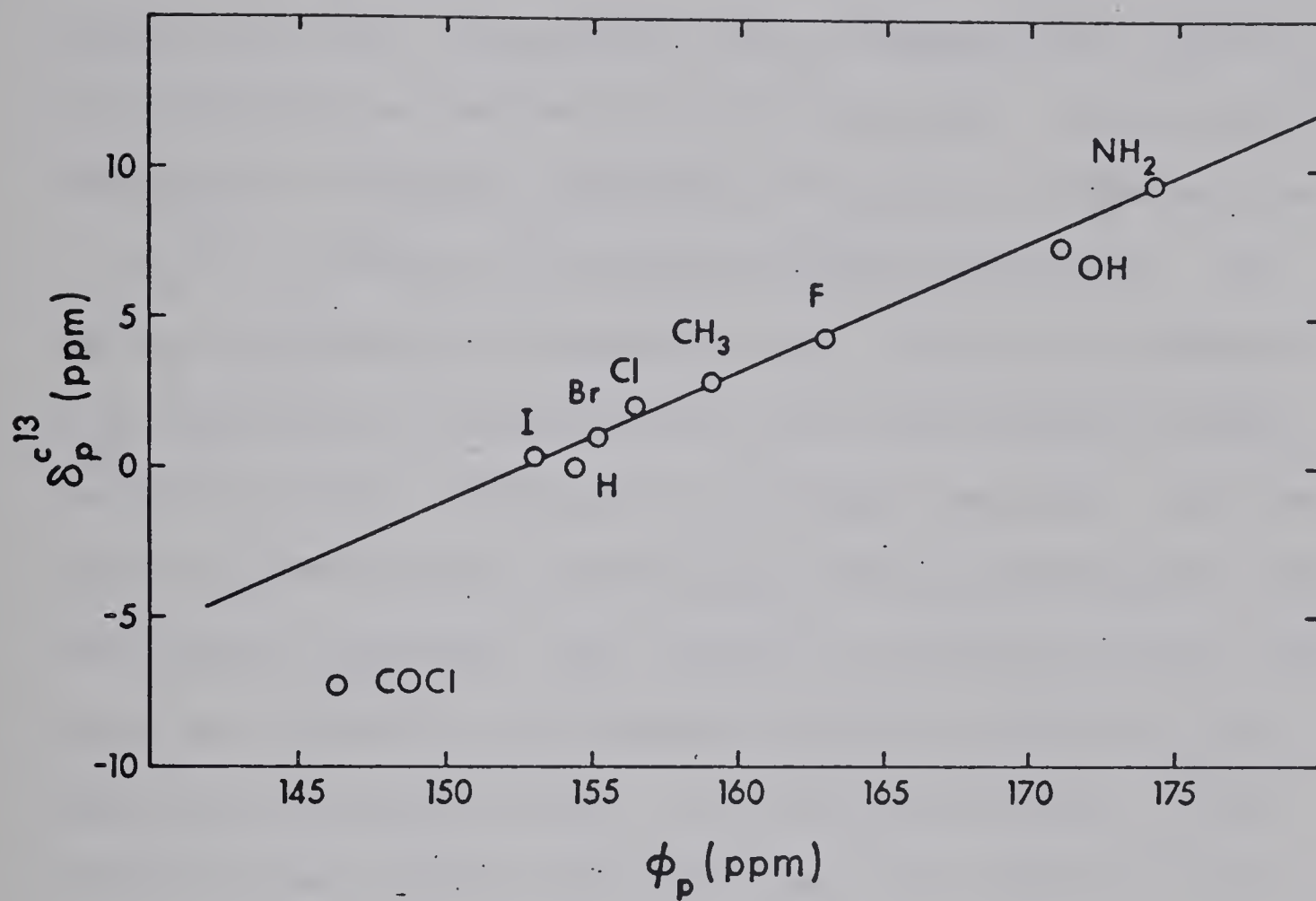


Figure 18. The relationship of the chemical shift of the para fluorine in certain pentafluorophenyl derivatives (ϕ_p) to the chemical shift of the para carbon in corresponding phenyl derivatives (δ_p^{13C}).

mainly from the resonance effect of a substituent.

Apart from molecular orbital calculations of electron density, the only quantitative treatment of substituent effects has been through the use of Hammett-Taft substituent functions as derived from reactivities. Taft modified the original Hammett substituent function σ , to the form $\sigma = \sigma_R^O + \sigma_I$ where σ_R^O is the resonance parameter (47) and σ_I the inductive parameter (48). The use of Hammett-type functions in correlations with spectroscopic observations has been questioned on several grounds: (a) the Hammett functions are based upon chemical reactivity which are heavily dependent upon effects to the transition state which are temporary electromeric effects differing from those of the ground state: (b) they are derived from disubstituted phenyl compounds where the choice of reaction site may well change the relative effects from one substituent to another: (c) chemical shifts are often dependent upon physical effects such as magnetic anisotropy, which would not affect the chemical reactivity of the compound. However a relation between the π -interaction of the substituent and the $J_{24} - \phi_p$ plot would require at least an approximate correlation between the Hammett-Taft functions and ϕ_p and J_{24} values.

In the work of Taft et al., (49) the following relation was found for the F^{19} chemical shifts of para-

fluorophenyl derivatives

$$\delta_p^F = -29.5 \sigma_R^O - 7.1 \sigma_I + 0.60$$

while for the F^{19} chemical shifts of metafluorophenyl derivatives, (45)

$$\delta_m^F = -7.1 \sigma_I + 0.60.$$

The seemingly entirely fortuitous agreement in the σ_I coefficients and constants in these two equations resulted in $\delta_p^F - \delta_m^F$ being dependent upon only the resonance parameter. This correlation was extended to organometallic compounds by Parshall (50) who studied the interaction of platinum with the ligand X in para and meta-fluorophenyl-platinum(II) complexes of the type $FC_6H_4PtX[(C_2H_5)_3P]_2$.

The pentafluorophenyl system has obvious advantages over the monofluorophenyl systems in that both para and meta chemical shifts can be determined from a single sample. This necessarily means that they have been extracted from identical chemical environments. This is certainly not the case in the monofluoroderivatives where the bonding throughout the molecule is different for the para-fluorophenyl compound compared with the meta-fluorophenyl compound. Thus in the pentafluorophenyl compound there is no change resulting from different interactions between substituent and observation site (the F^{19} nucleus). The presence of additional nmr information in the form of

coupling constants is a further advantage.

As can be seen in Equations 7 and 8 of Table IX, the pentafluorophenyl chemical shifts are related to the σ_R^O and σ_I functions in a similar yet quantitatively different way to the mono-fluoro shifts of Taft. Similar equations have already been derived by Lawrenson (16). A different choice of chemical shift values (Table III), due to averaging results and standardizing conditions of measurements, has led to slightly different coefficients in these equations as compared to those of Lawrenson. A third equation (Equation 9, Table IX) is now added relating J_{24} to these functions as shown in Figure 19. It should be noted that J_{24} relates best to almost the same combinations of the Taft functions as does $\phi_p: (\sigma_R^O + 0.33 \sigma_I)$ for ϕ_p versus $(\sigma_R^O + 0.30 \sigma_I)$ for J_{24} . It can also be seen that ϕ_m forms a poorer relationship--as shown by a lower $(r_{xy})^2$ value--although the RMS value is smaller, a result of the smaller range of ϕ_m values found. In contrast to monofluoro shifts, the coefficients of the σ_I terms are not the same for ϕ_p as for ϕ_m . Subtraction therefore does not eliminate σ_I , and the use of $\phi_p - \phi_m$ as a criterion of resonance interaction (17,22) has no theoretical justification. Some improvement may result from the use of $\phi_p - \phi_m$, however, since the difference in shifts eliminates errors such as those due to non-

TABLE IX

Equations Derived by Least Mean Square Analysis^a, Relating ϕ_p , ϕ_m and J_{24} to the Taft Functions, σ_R^o and σ_I^b .

Equation	$(r_{xy})^2$	G-O-F	RMS	Pts
1 $\phi_p = -52.28 \sigma_R^o + 148.74$	0.85	FAIR	3.6	8
2 $\phi_m = -10.75 \sigma_R^o + 160.56$	0.54	BAD	1.6	8
3 $J_{24} = 22.26 \sigma_R^o + 3.81$	0.87	FAIR	1.5	8
4 $\phi_p = -24.22 \sigma_I + 163.78$	0.28	V.BAD	7.4	11
5 $\phi_m = -8.31 \sigma_I + 164.64$	0.54	BAD	1.5	11
6 $J_{24} = 10.22 \sigma_I - 2.24$	0.25	V.BAD	3.4	11
7 $\phi_p = -49.05 \sigma_R^o - 16.00 \sigma_I + 153.72$	0.99 ₉	V.GOOD	0.91	8
8 $\phi_m = -9.36 \sigma_R^o - 6.91 \sigma_I + 162.71$	0.93	GOOD	0.65	8
9 $J_{24} = 21.00 \sigma_R^o + 6.21 \sigma_I + 1.88$	0.98	GOOD	0.56	8

^a $(r_{xy})^2$ is the square of the correlation coefficient; G-O-F is the name given to the goodness of fit (p.39) ; RMS is the root mean square deviation and Pts is the number of points used in the analysis.

^b Values of σ_R^o and σ_I used are found in Appendix C.

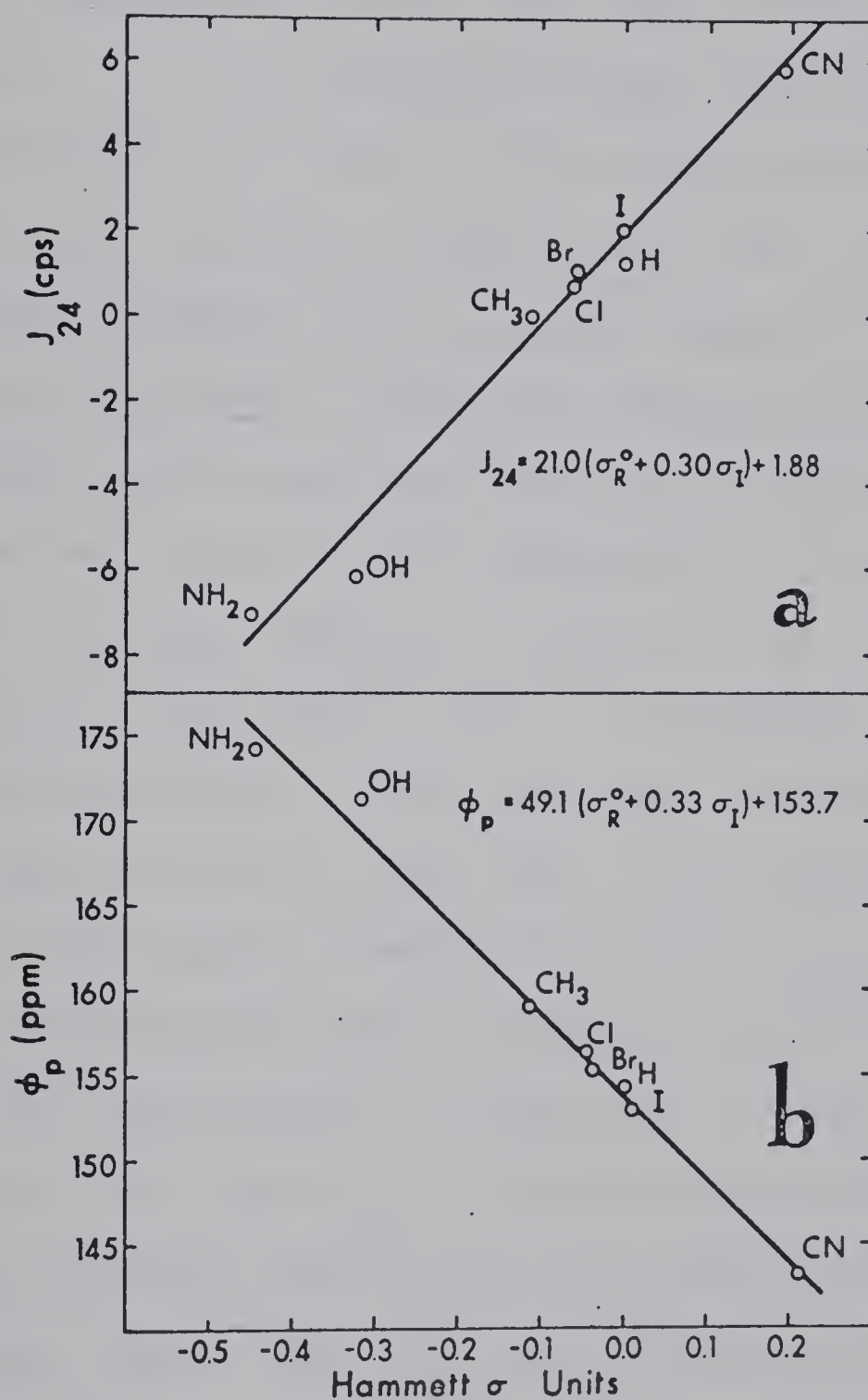


Figure 19. The relationship of J_{24} and ϕ_p to the best combination of the Hammett-Taft parameters σ_R° and σ_I .

standardization of the reference and varying bulk susceptibilities of the solvents. As can be seen from Equations 7 and 9 of Table IX and coefficient of the resonance parameter is considerably larger than that of the inductive parameter. It is not surprising then, that ϕ_p and J_{24} can separately be related to σ_R^O alone, giving reasonable straight lines as shown by Equations 1 and 3 of Table IX. This is the algebraic way of saying that both ϕ_p and J_{24} are sensitive mainly to resonance interactions.

As can also be seen from Equations 7, 8 and 9 in Table IX, , the nmr parameter most affected by the inductive function σ_I is ϕ_m . However, the plot of ϕ_m with σ_I (Equation 5) is too poor a fit to a straight line to be considered meaningful. While the Taft functions σ_R^O and σ_I have been related in this way, it is interesting to find that the original Hammett functions, σ_{para} and σ_{meta} , can be related both separately and in combination, to the three nmr parameters (Equations 1-9 of Table X and Figure 20). The $(r_{xy})^2$ values are in each case only slightly inferior than those found for the Taft function.

Further support for the π donor-acceptor relationship of Figure 17 is found in the order of the halogens in the $J_{24} - \phi_p$ plot. In general, resonance and inductive effects act in the same direction. However, the resonance effects of the halogens act in the opposite direction to the in-

TABLE X

Equations Derived by Least Mean Square Analysis^a Relating ϕ_p , ϕ_m and J_{24} to the Hammett Functions σ_{para} and σ_{meta} ^c

Equation ^b	$(r_{xy})^2$	G-O-F	RMS
1 $\phi_p = -22.24 \sigma_{para} + 159.47$	0.91	GOOD	2.6
2 $\phi_m = -5.41 \sigma_{para} + 162.91$	0.88	FAIR	0.7
3 $J_{24} = 10.04 \sigma_{para} - 0.495$	0.91	GOOD	1.2
4 $\phi_p = -30.5 \sigma_{meta} + 164.0$	0.58	BAD	5.6
5 $\phi_m = -8.58 \sigma_{meta} + 164.3$	0.76	POOR	1.1
6 $J_{24} = 13.45 \sigma_{meta} - 2.48$	0.56	BAD	2.6
7 $\phi_p = 22.92 \sigma_{meta} - 34.41 \sigma_{para} + 155.51$	0.97	GOOD	1.5
8 $\phi_m = -1.06 \sigma_{meta} - 4.85 \sigma_{para} + 163.10$	0.88	FAIR	0.7
9 $J_{24} = -12.06 \sigma_{meta} + 16.44 \sigma_{para} + 1.59$	0.99	GOOD	0.4

^a $(r_{xy})^2$ is the square of the correlation coefficient; G-O-F is the name given to the goodness of fit (p. 39); RMS is the root mean square deviation.

^bEach equation is derived from eleven points.

^cValues of σ_{para} and σ_{meta} used are found in Appendix C.

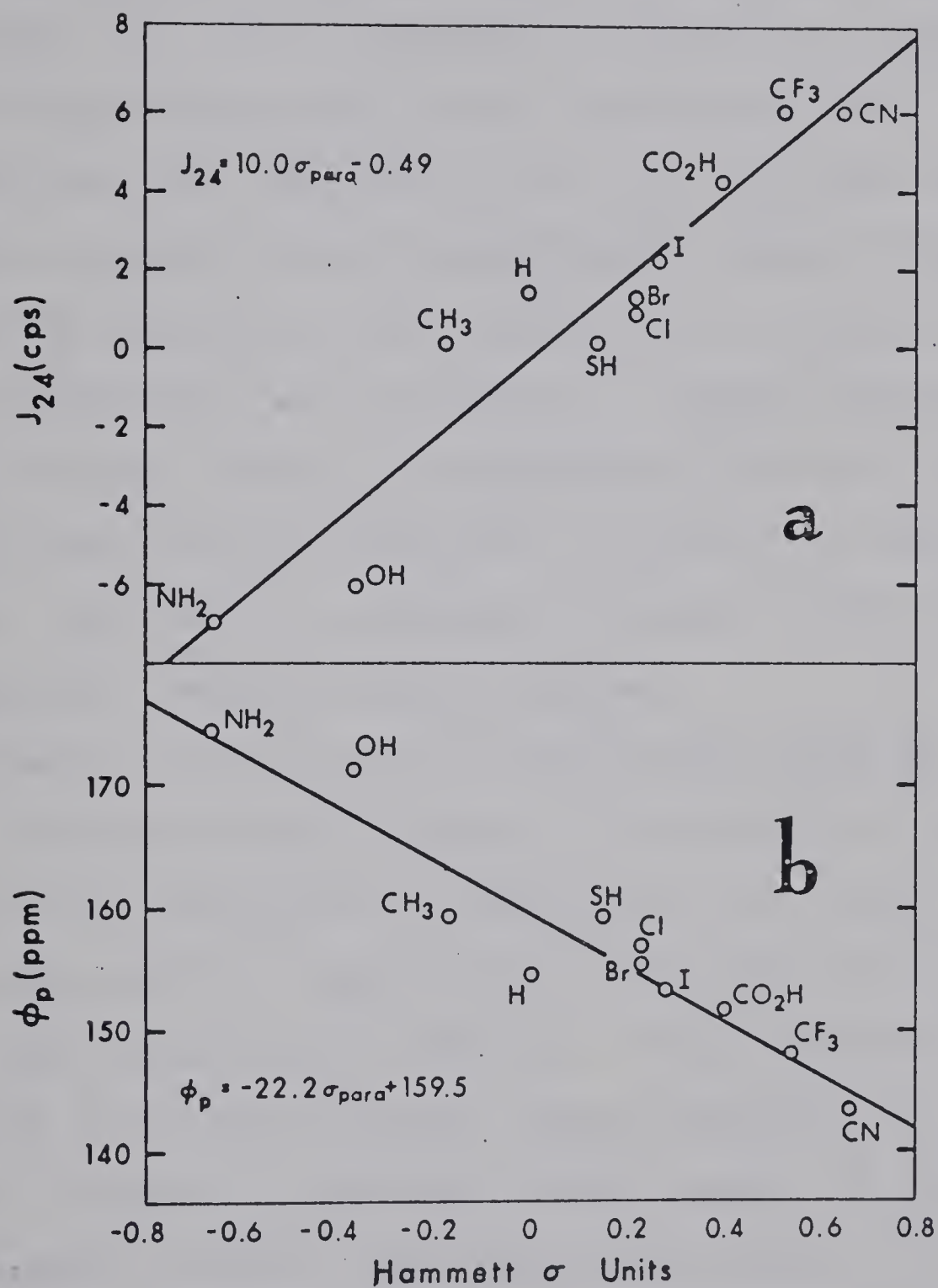
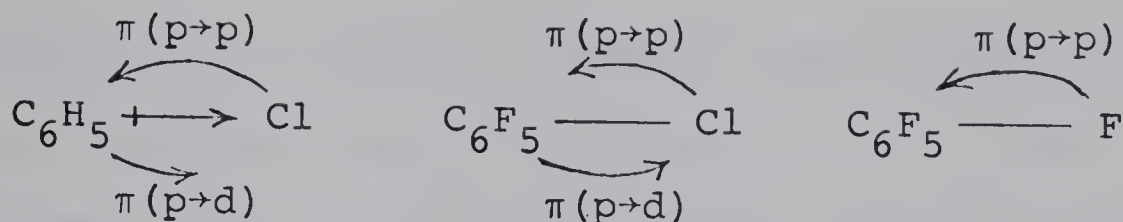


Figure 20. The relationship of J_{24} and ϕ_p to the Hammett parameter σ_{para} .

ductive effects (51). The order of the halogen substituents in the $J_{24} - \phi_p$ plot ($F > Cl > Br > I$ in donor strength) agrees with their relative order of π -donation as found from their σ_R^O values determined originally by linear free energy relationships using reactivities (52). The halogens are well separated on the $J_{24} - \phi_p$ plot with fluorine nearest the well established π donors ($-NH_2$) and iodine nearest the well established π acceptors ($-CN$). This establishes that the ordering is mainly dependent upon resonance effects; an appreciable inductive contribution would cause the halogens to close up in the $J_{24} - \phi_p$ plot, and lead to a complete inversion of the order if inductive effects became dominant.

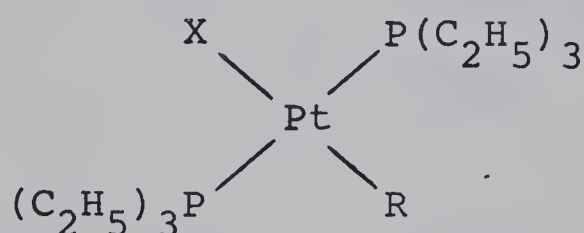
However, in the case of substituents which may involve partial multiple bonding to the ring (ie., back-donation of π electrons in addition to the σ bond), the σ_R^O values will not necessarily be the same for systems other than disubstituted benzenes. Thus, although the ordering of the four halogens among themselves in π -donor strength is the same in both phenyl and pentafluorophenyl systems, their positions relative to substituents with negligible π effects ($-CH_3$ and $-H$) are not. In the phenyl series, the halogens are essentially weak π donors, with σ_R^O values becoming more negative in the series $H < I < CH_3 < Br < Cl < F$; This is the same

order found by Taft in the F^{19} nmr studies on monofluorophenyl derivatives mentioned previously. However, halogens as substituents on the pentafluorophenyl ring appear to be much weaker π donors; the order of π donor strength is $I < H < Br < Cl < CH_3 < F$, so that with the exception of fluorine they might be considered π acceptors. The different character of the halogens in the C_6H_5X and C_6F_5X systems seems to relate to the polarity of the ring-halogen σ bond. In the halobenzenes, this bond will be rather highly polar with the halogen atom negative. This polarity will favor the transfer or back-donation of halogen lone pair electrons to the benzene ring so that the halogens will appear as π donors. This viewpoint is similar to the synergic mechanism attributed to the metal ligand bond in coordination chemistry (53). In the penta-fluorophenyl system, however, the relatively high electronegativity of the C_6F_5 group will diminish the polarity of the ring-substituent σ bond, and the tendency of the halogen to donate its lone pairs to the ring will be correspondingly reduced. Fluorine still appears as a π donor but in the other halogens where vacant valence shell d orbitals are available, the balance is shifted to a net π -acceptor property; schematically the proposed bonding might be represented:



where the symbol \longleftrightarrow represents a σ bond polarized in the sense shown.

The π character of halogens has been determined in two other series; the platinum (II) complexes of the type



where for series I: $\text{R} = \text{C}_6\text{F}_5$ series II: $\text{R} = \text{C}_6\text{H}_4\text{F}$ and $\text{X} =$ halogen or other anionic ligands. The halogens were found to act as π acceptor in series I (17) although as π donors in series II (50). This is a further instance where the π character of the halogens may vary, depending upon their chemical environment. It should be noted that whereas the overall trend of π donor or acceptor character can be inferred using the method of Parshall for series II, the significance of small trends within the series should not be overrated. The π -acceptor parameter is obtained as the difference between two fluorine chemical shifts, and for CH_3 , Cl, Br and I, covers a range of only 0.2 ppm. This is comparable to the vari-

TABLE XI

Tables of π -acceptor Criteria^a for Ligands (X) in the Series $\text{FC}_6\text{H}_4\text{Pt}[\text{P}(\text{CH}_2\text{CH}_3)_3]_2\text{X}$ as Determined in the Two Solvents Acetone and Cyclohexane.

Acetone		Cyclohexane	
-CN	0.7	-CN	0.86
-SnCl ₃	0.6	-C \equiv C-C ₆ H ₅	0.4
-C \equiv C-C ₆ H ₅		-C ₆ H ₅	0.2
-C ₆ H ₅	0.3	-SCN	0.14
-C ₆ H ₄ F (meta)		(or -NCS)	
-C ₆ H ₄ F (para)		-C ₆ H ₄ F (para)	0.0
-SCN	0.2	-CH ₃	
(or -NCS)			
-OCN	0.0	-OCN	-0.3
(or -NCO)		(or -NCO)	
-CH ₃		-Cl	
		-Br	
-Br	-0.1	-I	
-Cl	-0.2		
-I			

^aTaken from Reference (50), which quotes order from results in acetone, but not cyclohexane. π -acceptor criterion is difference in chemical shifts of para and meta fluorophenyl derivatives.

ation that solvent effects can introduce, a fact which is apparent when the π -acceptor parameter is calculated from Parshall's results in cyclohexane. Thus the precise ordering of the halogens is different in cyclohexane than in acetone (Table XI), although in both solvents, they appear to be π donors to platinum in the monofluorophenyl systems.

In conclusion, the values of J_{24} and ϕ_p as found from the pentafluorophenyl group seem to provide a useful guide to electronic behavior within a larger molecule, in particular, the π -electron interaction. It should be possible to use this guide to elucidate the bonding in a variety of systems. In the following Chapter, its use is demonstrated with reference to phosphines, group IV organometallic derivatives of pentafluorophenol, pentafluorothiophenol and pentafluoroaniline.

CHAPTER IV

APPLICATIONS

This chapter describes the application of the $J_{24} - \phi_p$ relationship to selected series of compounds.

1. The separation of first row substituent groups from their second and third row congeners. The $J_{24} - \phi_p$ relationship which has been derived in the previous Chapter is now redrawn in Figure 21. Twelve extra points are plotted whose J_{24} and ϕ_p values will be found in the accompanying tables in this Chapter. The common organic substituents and the π donor-acceptor relationship are indicated in the figure.

Examination of Figure 21, reveals a marked separation of compounds depending on whether a first-row element is bonded to the pentafluorophenyl ring, or whether the substituent is attached through an element from the second or third periodic groups. This may be clearly seen for substituents involving main groups V, VI, and VII. The separation is evidently due to the absence of vacant d orbitals in the valence shell of first row elements. Hence amines, as represented by the NH_2 group, act as π donors, while phosphines show weak to strong acceptor properties; donation of the phosphorus lone pair to the C_6F_5 ring is apparently more than countered by a $\pi(\text{p} \rightarrow \text{d})$ withdrawal of electrons from the ring. Simil-

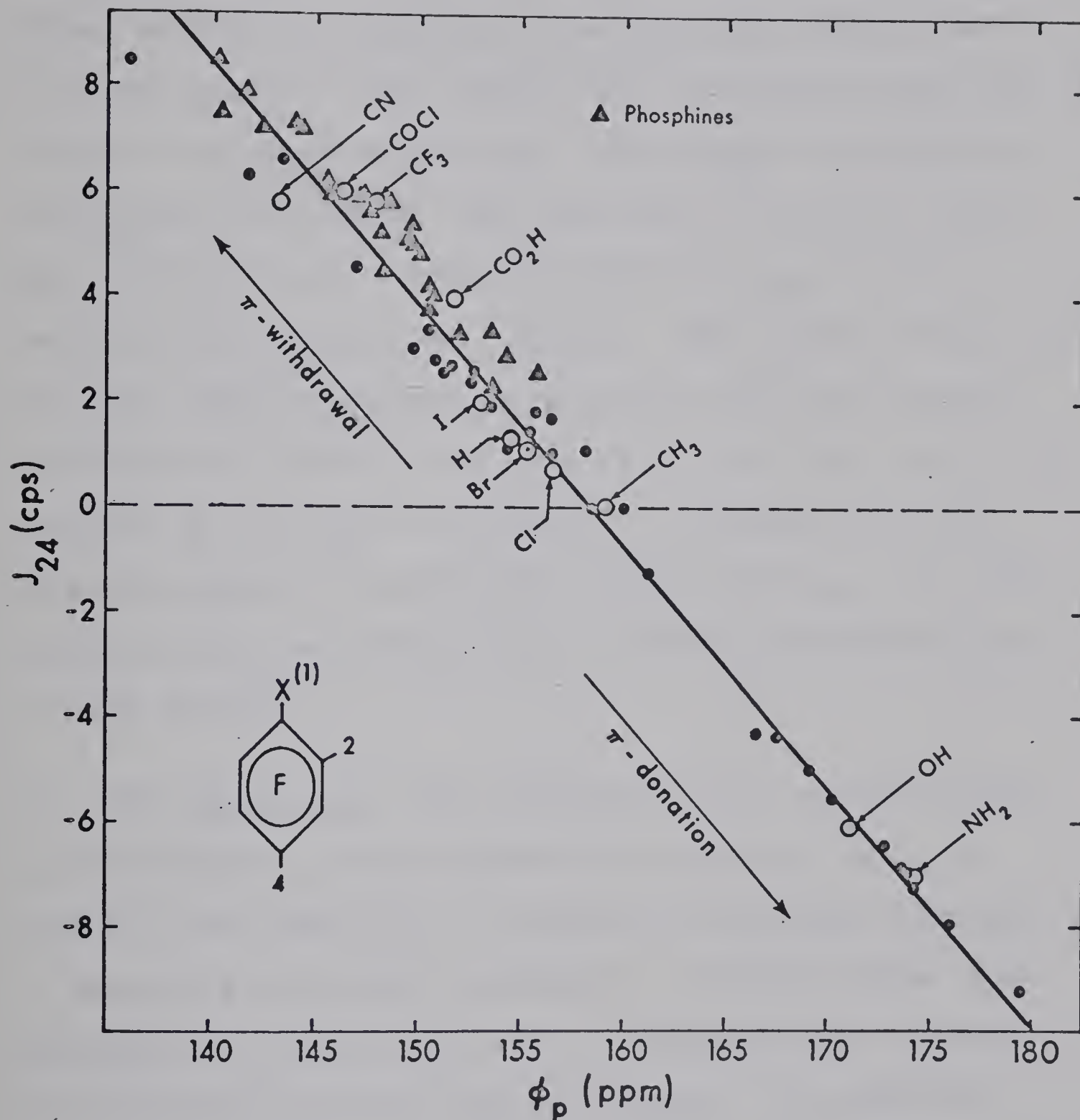


Figure 21: The $J_{24}-\phi_p$ relationship for 73 points; the common organic substituents are labelled.

arly the $\pi(p \rightarrow p)$ donation that causes the OH group to be a strong donor is counterbalanced in C_6F_5SH by donation of ring π electrons to the vacant 3d orbitals of sulfur. Thus, as shown in Figure 23, the -SH group shows a net π effect close to zero, while other -SR derivatives have slight π -acceptor properties. The halogen substituents also show this effect. The position of fluorine itself as inferred from the chemical shift of C_6F_6 is well separated from the other halogens. One notable exception to this trend of separation of first and later row substituents is found in the case of CF_3 and SiF_3 ; here, CF_3 appears to be almost as strong a π acceptor as SiF_3 , and the points lie relatively close on the $J_{24} - \phi_p$ plot. This interesting anomaly will be further discussed later in the Chapter.

2. The Phosphines. The positions of all 29 derivatives with phosphorus as the substituent atom are shown in Figure 21 and Table XII. In general they range from weak π acceptors to strong π acceptors. Figure 22 shows the phosphines in detail and with reference to that figure the following results are of interest. It should be noted that the points are identified in groups; the mono-pentafluorophenyl derivatives are all labelled above the line, the bis- and trispentafluorophenyl derivatives are labelled in groups below the line.

TABLE XII

Para-fluorine Chemical Shifts, ϕ_p , and the Ortho- Para-
Fluorine Coupling Constant, J_{24} , of Various Penta-
fluorophenylphosphines

	ϕ_p^a	J_{24}^b	Ref. ^c
$C_6F_5 - POF_2$	140.2	8.6	A
$C_6F_5 - P(C_6H_5)_2HCl$	140.4	7.5	A
$C_6F_5 - P(C_6H_5)_2BCl_3$	143.8	7.3	A
$C_6F_5 - PCl_2$	145.4	6.2	A,B
$C_6F_5 - P(C_6H_5)_2O$	147.3	5.9	A
$C_6F_5 - PF_2$	147.4	5.9	B
$C_6F_5 - P(C_6H_5)_2S$	148.6	5.8	A
$C_6F_5 - PCl N(CH_3)_2$	149.6	5.4	B
$C_6F_5 - P(C_6H_5)_2W(CO)_5$	149.2	5.2	A
$\{C_6F_5P(C_6H_5)_2\}_2PdCl_2$	149.2	5.1	A
$C_6F_5 - P(C_6H_5)_2Fe(CO)_4$	149.5	5.0	A
$C_6F_5 - P(C_6H_5)_2Cr(CO)_5$	149.5	5.0	A
$C_6F_5 - P(C_6H_5)_2Mo(CO)_5$	150.0	4.8	A
$C_6F_5 - P(C_6H_5)_2$	150.6	4.0	A
$C_6F_5 - P(CH_2CH_3)_2$	153.5	3.3	B
$C_6F_5 - P(CH_3)_2$	154.2	2.9	A,B
$C_6F_5 - PH_2$	153.7	2.3	B
$C_6F_5 - P[N(CH_3)_2]_2$	155.7	2.6	B
contd.....			

TABLE XII (contd.)

	ϕ_p^a	J_{24}^b	Ref. ^c
$(C_6F_5)_2POF$	141.5	7.9	A
$(C_6F_5)_2PCl$	147.5	5.6	A,B
$(C_6F_5)_2P(C_6H_5)Mo(CO)_5$	148.1	5.2	A
$(C_6F_5)_2PC_6H_5$	150.5	4.2	A
$(C_6F_5)_2PH$	150.5	3.8	B
$(C_6F_5)_2PN(CH_3)_2$	152.1	3.3	B
$(C_6F_5)_3PO$	142.4	7.2	A
$(C_6F_5)_3PS$	144.3	7.2	A
$(C_6F_5)_3PF_2$	146.0	6.0	A
$(C_6F_5)_3P$	147.7	4.5	A

a) in ppm based on the scale: $C_6F_6 = 163.0$ ppm upfield from $CFCl_3$.

b) in cps.

c) A this work; B, Reference (22)

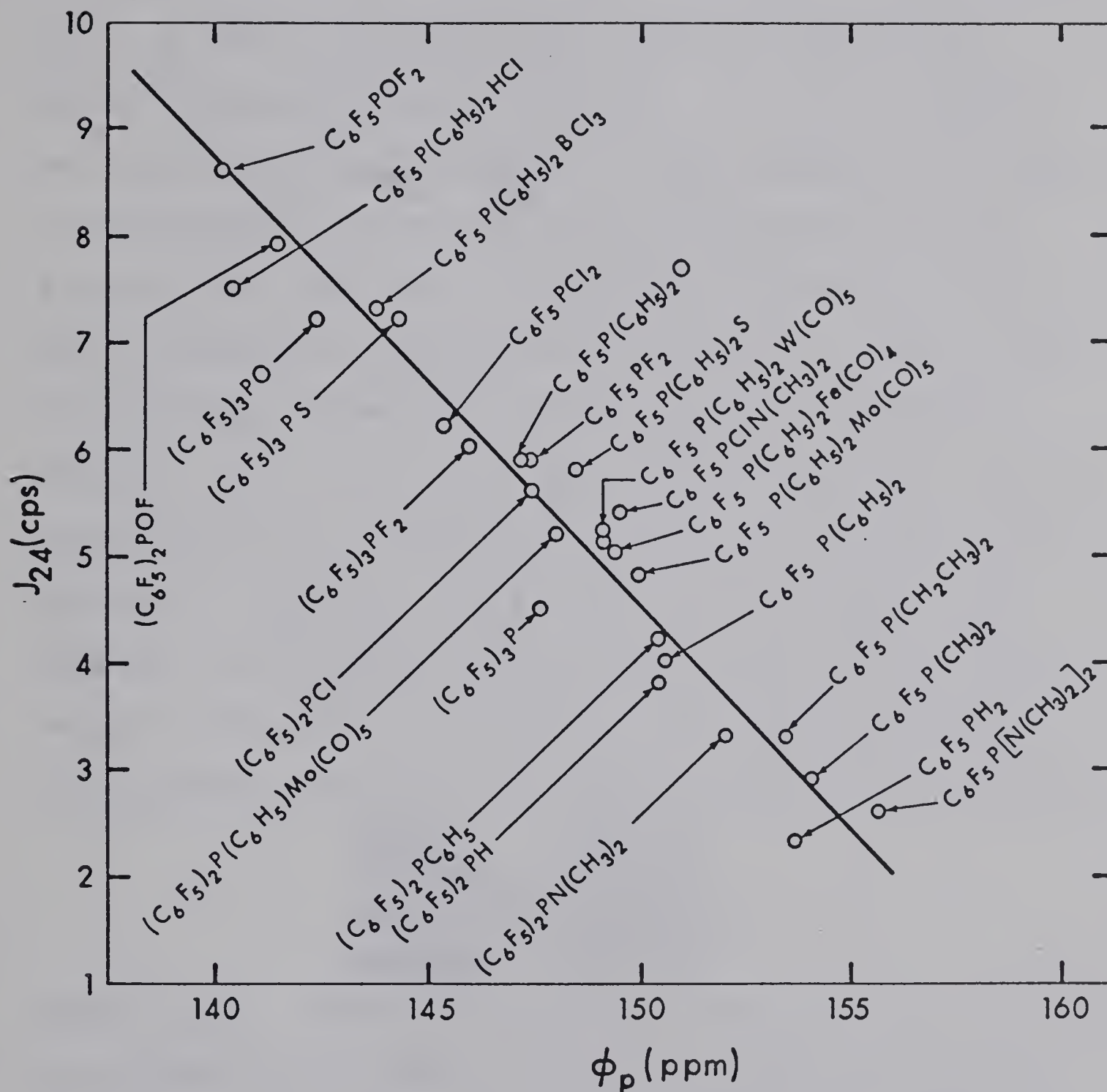
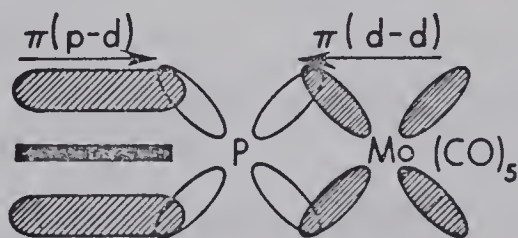


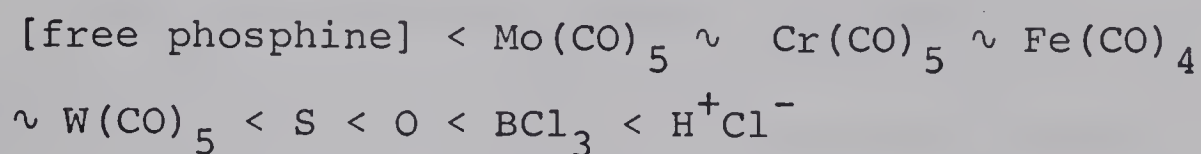
Figure 22: The $J_{24} - \phi_p$ relationship for 29 pentafluorophenylphosphines.

Within the phosphines, there can be distinguished a number of smaller series which form a regular order and can be explained in terms of π -bonding orbitals. The $J_{24} - \phi_P$ plot illustrates the bonding in the series pentafluorophenyldiphenylphosphine, its metal carbonyl and boron trichloride adducts. These compounds increase in withdrawal of electrons from the pentafluorophenyl ring in that order due to the partial donation of lone pair electrons on phosphorus to the metal or boron atom. If the boron trichloride adduct represents an almost complete loss of the lone pair in a σ bond, $P \rightarrow B$, then we rationalize the intermediate position of the metal carbonyls as a similar σ bond, $P \rightarrow M$, together with a back donation of electrons from the transition metal to the vacant d orbitals on phosphorus. The net result is an intermediate withdrawal of electrons from the pentafluoro-



phenyl ring. Figure 22 also shows that when the lone pair on phosphorus is bonded to oxygen or sulfur the result is again a withdrawal of electrons from the pentafluorophenyl ring which is stronger than that in the metal carbonyl adduct but weaker than the boron trichloride adduct. It can also be seen that formation of the phosphonium chloride causes a more complete loss of electrons than in

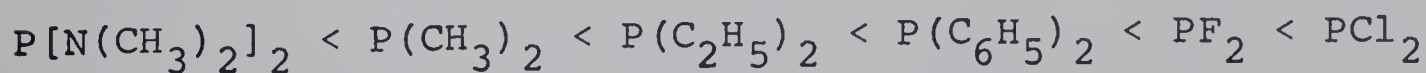
the formation of the BCl_3 adduct. Hence in the series of pentafluorophenyldiphenylphosphines, $\text{C}_6\text{F}_5\text{P}(\text{C}_6\text{H}_5)_2\text{X}$, the order of increasing withdrawal of electrons as experienced by the pentafluorophenyl ring is:



A similar increase in π -withdrawal is found when pentafluorophenylphosphorus difluoride is oxidized to the corresponding oxyfluoride. When the lone pair in tris-pentafluorophenylphosphine is bonded to oxygen or sulfur, an increase in π -withdrawal from the benzene rings is again found. The lone pair can also be effectively removed when the phosphorus expands its coordination to five in the compound tris-pentafluorophenylphosphorus difluoride. The order of withdrawal of π electrons from the benzene ring is:



The $J_{24} - \phi_p$ plot also reveals the order of π acceptor power of X in the series $\text{C}_6\text{F}_5\text{X}$ as



3. The oxygen and sulfur group IV metal compounds. Figure 23 and Table XIII give the J_{24} and ϕ_p values for the series of compounds:

TABLE XIII

Para-fluorine Chemical Shifts, ϕ_p , and the ortho-para-
Fluorine Coupling Constant, J_{24} , of Series of Group
IV Metal Sulfur and oxygen compounds.^a

	ϕ_p^b	J_{24}^c
$C_6F_5 - S Si(CH_3)_3$	155.3	1.4
$C_6F_5 - S Ge(CH_3)_3$	156.5	1.0
$C_6F_5 - S Sn(CH_3)_3$	158.4	0
$C_6F_5 - S Pb(CH_3)_3$	160.0	0
$C_6F_5 - SH$	159.1	0
$C_6F_5 - S Si(C_6H_5)_3$	155.7	1.8
$C_6F_5 - S Ge(C_6H_5)_3$	156.5	1.7
$C_6F_5 - S Sn(C_6H_5)_3$	158.1	1.1
$C_6F_5 - O Si(CH_3)_3$	167.6	-4.4
$C_6F_5 - O Ge(CH_3)_3$	170.3	-5.6
$C_6F_5 - O Sn(CH_3)_3$	174.2	-7.3

contd.....

TABLE XIII (contd.)

	ϕ_p^b	J_{24}^c
$C_6F_5 - OH$	171.2	-6.1
$C_6F_5 - O Si (C_6H_5)_3$	166.5	-4.3
$C_6F_5 - O Ge (C_6H_5)_3$	169.2	-5.0
$C_6F_5 - O Sn (C_6H_5)_3$	172.8	-6.4
$C_6F_5 - O Pb (C_6H_5)_3$	176.1	-8.0

^aAll results presented here are from this work, except C_6F_5OH , Reference (15).

^bin ppm based on the scale: $C_6F_6 = 163.0$ ppm upfield from $CFCl_3$.

^cin cps.

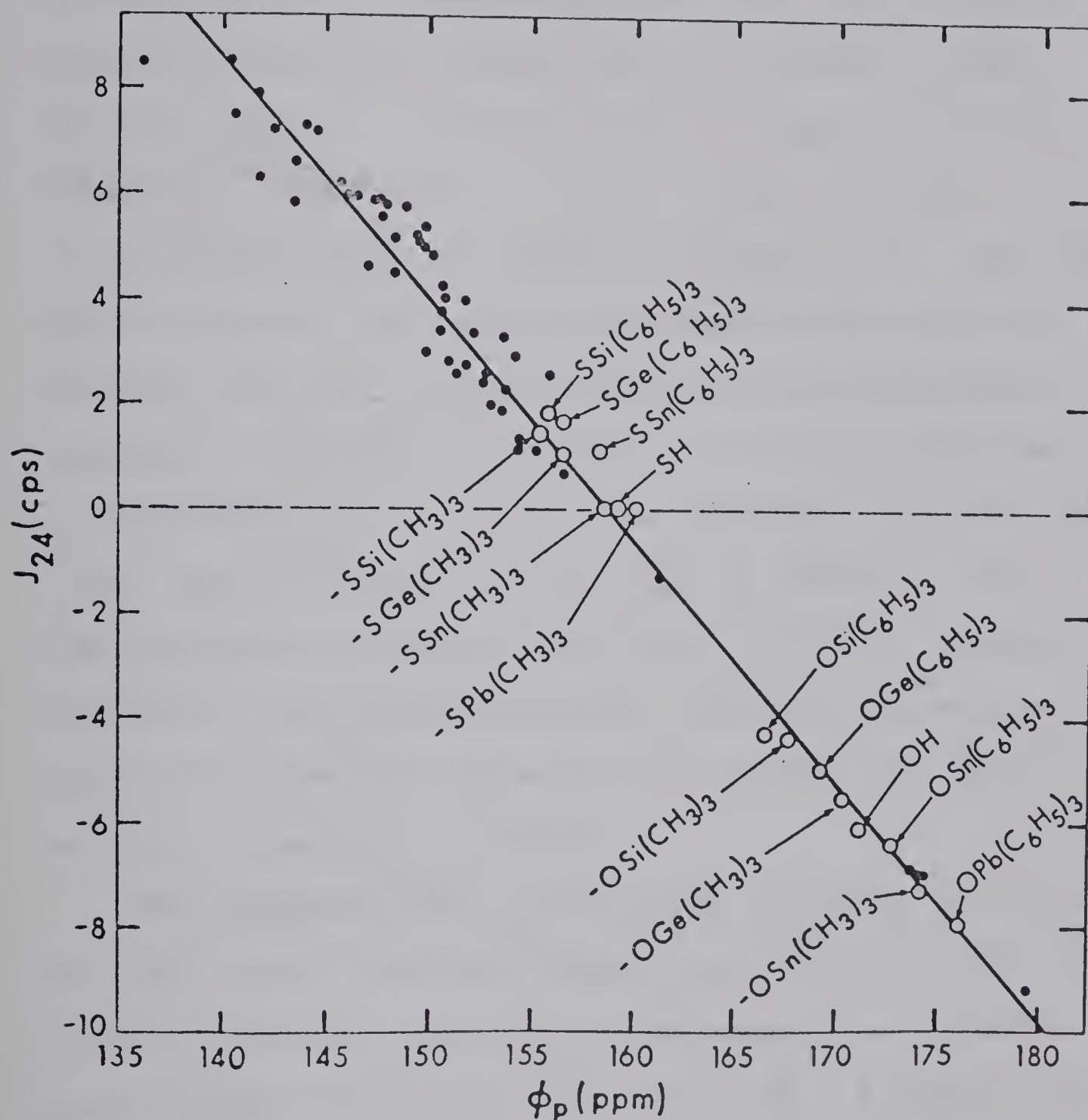
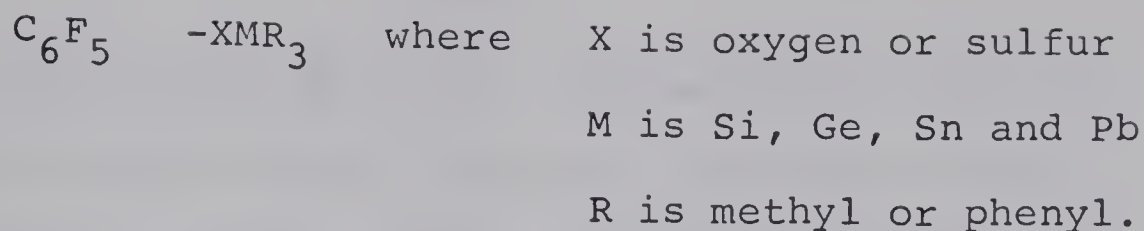


Figure 23. The $J_{24} - \phi_p$ relationship for compounds of the type $\text{C}_6\text{F}_5\text{-XMR}_3$ where $\text{X} = \text{O}$ or S , $\text{M} = \text{Si}$, Ge , Sn and Pb , $\text{R} = \text{CH}_3$ or C_6H_5 .



The separation of sulfur compounds from the analogous oxygen compounds has already been attributed to back donation of ring π electrons to the vacant d orbitals of sulfur; this reduces the net π donor strength of sulfur substituents in general to almost zero. The lone pairs on sulfur and oxygen have two possible modes of bonding: they can interact with the pentafluorophenyl causing an increase in π -electron density in the ring, or with the group IV metal, when possible. In the latter case, ring π -electron density will be reduced. Thus, the two competing bonding possibilities will have opposite effects on the pentafluorophenyl ring which provides a means of estimating the extent of π bonding of oxygen or sulfur to the group IV element.

The observed order of the group IV metals is the same in both oxygen and sulfur series, and indicates that the order of ease of formation of the oxygen (or sulfur) — metal double bond is $\text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$. A possible explanation of this would be that the overlap between the group IV vacant d orbital and the group VI lone pairs is strongest for silicon and decreases to lead. Attempts to prepare the trimethyl carbon (tert-butyl) derivatives

have not been successful (54). These points would be extremely valuable since they would represent cases in which double bond formation by the group IV element was possible only with the benzene ring. The points for the phenol and thiophenol are available, however, and their positions within the two series are of some interest. The phenol derivative is midway between germanium and tin, which would indicate that while silicon and germanium are π acceptors, tin and lead are π -donors relative to H

These estimates of the π acceptor properties of the group IV metals are in accord with previous studies (55,56,57). The electron donating properties of tin and lead were explained in terms of electronegativities and inductive effects. However, in the light of this study, it may well be possible that tin and lead are exhibiting π -donor properties. This may be due to the 3d and 4d orbitals which are vacant in silicon and germanium but are filled orbitals in tin and lead giving the π -donor effect.

Similarly for the sulfur compounds, the thiophenol is close to tin and lead (Figure 23) and silicon and germanium act as π -acceptors. Thus the π -acceptor properties of germanium are much stronger with sulfur than with oxygen, which also agrees with the previous studies of C-D stretching frequencies in mixtures of

base and deuteriochloroform and also the nmr proton deshielding in chloroform (57).

4. The pentafluoroaniline derivatives. The J_{24} and ϕ_p values of several pentafluoroaniline derivatives are presented here with results that are pertinent to the current re-examination of the concept of nitrogen-silicon π bonding (58,59,60). The planarity of trisilylamine (and, presumably, the sp^2 hybridization of the σ bonds of nitrogen) has long been explained in terms of nitrogen to silicon (p \rightarrow d) π -bonding. It was assumed by many that this effect on the σ -hybridization and geometry of nitrogen would be a necessary consequence of (p \rightarrow d) π -bonding in other silylamines. Thus it was surprising when the value of $J(N^{15}-H)$ in $C_6H_5 N^{15}HSi(CH_3)_3$, 76 cps (58), which was expected to increase with increased percentage of s character in the nitrogen σ orbitals, was but little changed from values reported for aniline itself, 78 cps (58). Double bond formation between nitrogen and silicon would presumably have resulted in sp^2 hybridization, giving higher $J(N^{15}-H)$ values, as in the case of the pyridinium ion (variously given as 98.7 and 90.5 cps) as opposed to sp^3 hybridization exemplified by the ammonium ion ($J(N^{15}-H) = 73.7, 73.2$ cps) (61,62,63). As was pointed out (59), the non-planar geometry inferred from coupling constant measurements did not exclude the

possibility of π -bonding between the lone pair and silicon d-orbitals, which would be possible even in a pyramidal silylamine. It was also suggested that the above argument notwithstanding, the hybridization used in the N-H bond need not change if the silicon gains double bond character at the expense of the benzene ring alone (64). In other words, this argument seems to imply that it would not matter to which atom the nitrogen donates its lone pair since the N-H hybridization is dependent only upon the total of the lone pair donation to both silicon and the benzene ring.

The need for a non-stereochemical means of investigating nitrogen-silicon π -bonding has been stressed (60); the approach suggested here may fill this need, since it depends only on the electron distribution as experienced by the pentafluorophenyl ring and not upon the geometry of the nitrogen, nor the nature of the remaining N-H bond.

It is evident from the Figure 24 and Table XIV and the -NH_2 group is a π -donor, the result of interaction of the lone pair with the pentafluorophenyl ring. Replacement of hydrogen by a group capable of π bonding with nitrogen should reduce donation to the pentafluorophenyl ring. Thus in the compound $\text{C}_6\text{F}_5\text{NH-B(C}_6\text{H}_5)_2$, where nitrogen to boron $(p \rightarrow p)\pi$ bonding is expected, donation to the pentafluorophenyl ring is much reduced, as shown in

TABLE XIV

Para-fluorine Chemical Shifts, ϕ_p , and the Ortho-Para fluorine Coupling Constant, J_{24} , for Some Pentafluoro-aniline Derivatives.

	ϕ_p^a	J_{24}^b	Ref. ^c
$C_6F_5 - N(H) B(C_6H_5)_2^d$	161.2	-1.3	A
$C_6F_5 - N(CH_3)_2^d$	166.2	-3.1	A
$C_6F_5 - N(H) CH_3$	173.8	-6.9	B
$C_6F_5 - N(H) Si(CH_3)_3$	174.1	-7.0	A
$C_6F_5 - NH_2$	174.3	-7.0	A,C
$C_6F_5 - N(H) Sn(CH_3)_3^d$	179.5	-9.2	A

^a
in ppm based on the scale: $C_6F_6 = 163.0$ upfield from $CFC1_3$.

^b
in cps.

^c
A, This work; B, Reference (15); C, Reference (16).

^d
Additional compounds which were not included in statistical analysis of Chapter III.

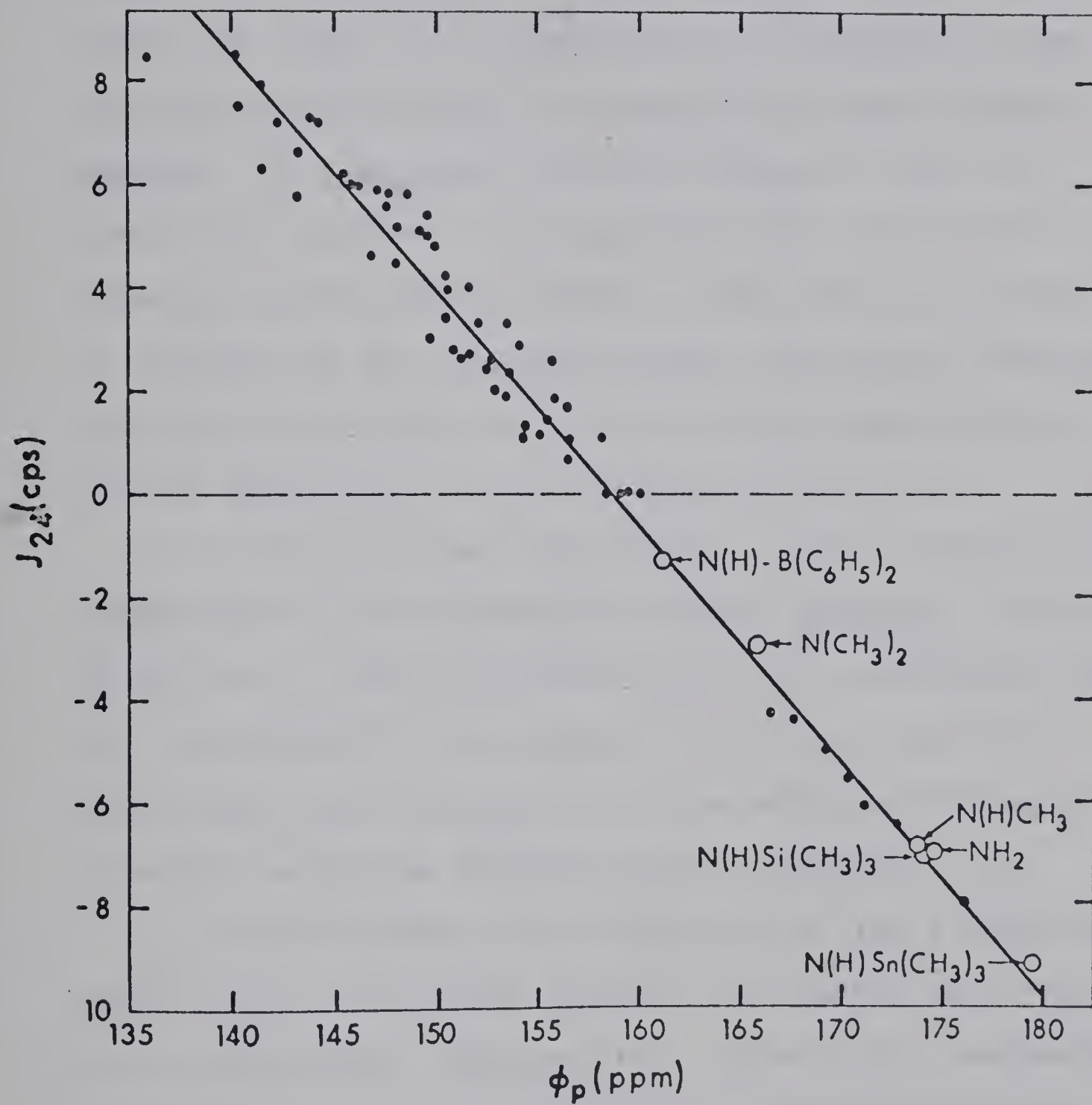


Figure 24. The $J_{24} - \phi_p$ relationship for pentafluoroaniline derivatives.

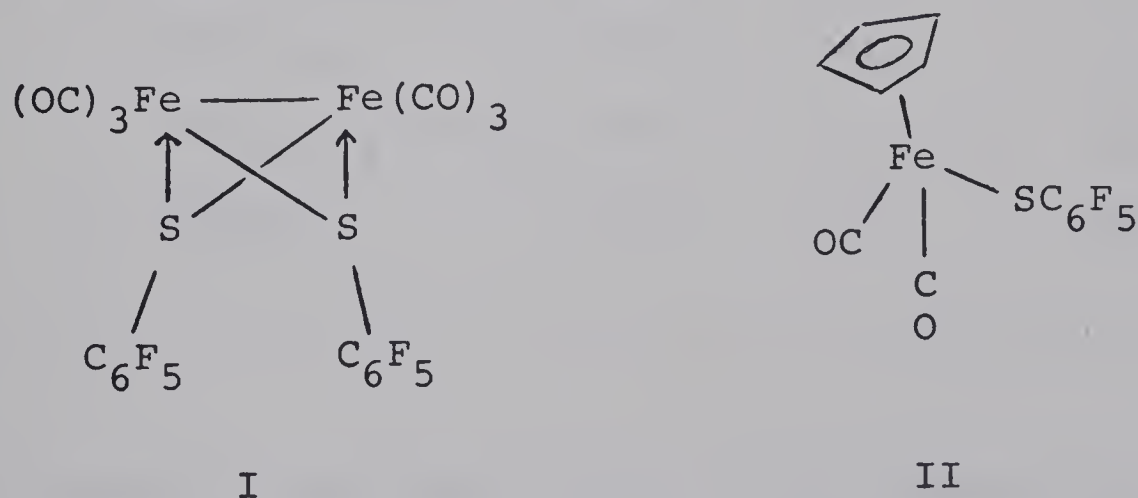
Figure 24. Surprisingly, however, substitution of hydrogen by a trimethylsilyl group does not change the π -donation to the ring. From this observation, we conclude that there is no appreciable π -character in the nitrogen-silicon bond in N-trimethylsilylpentafluoroaniline. This evidence therefore supports that of Randall and Zuckerman and questions the 'established' concept of Si-N double bonding. These results are also in contrast to the analogous oxygen and sulfur compounds, which have been shown by this and other techniques to involve appreciable double bonding with silicon.

It is also apparent from Figure 24 that substitution of hydrogen by the trimethyltin group enhances π donation to the ring; this is in accord with the decreasing order of π acceptance of the group IV metals as found for oxygen and sulfur and also with the enhanced basicity of organotin amines as found by other techniques (57).

It is of interest that π -donation by the N,N-dimethylamino group is less than that by the N-methylamino and amino substituents (Figure 24). This is not unexpected, since previous work has shown that steric interaction between the methyl groups and the ortho-fluorines inhibits resonance between the lone pair and the pentafluorophenyl ring (26,65).

5. Tin compounds. A series of pentafluorophenyltin compounds was studied. As can be seen in Table xv and Figure 25 , the range of values for ϕ_p and J_{24} was not large. Consequently, theoretical implications are less prominent. However, it is apparent that in going from $\text{Sn-C}_6\text{H}_5$ to Sn-Mn(CO)_5 , the acceptor strength of the tin atom decreases. This is consistent with the view that the tin-manganese bond is multiple in character, involving donation of electron density from filled 3d manganese orbitals to vacant 5d orbitals of tin (66). However the magnitude of the effect is small.

6. Two pentafluorothiophenoxy derivatives of iron carbonyl. Table XVI gives the J_{24} and ϕ_p values for the two compounds:



Comparing their positions on the $J_{24} - \phi_p$ plot in Figure 25, we find that the dimeric compound, I, with bridging sulfur shows the strongest withdrawal effect of all sulfur compounds examined, whereas the monomer, II, shows a

TABLE XV

Para-fluorine Chemical Shift (ϕ_p) and the Ortho- Para-
Fluorine Coupling constant (J_{24}) for Some Pentafluoro-
phenyl Tin Compounds.

		ϕ_p^a	J_{24}^b	Ref. ^c
$(C_6F_5)_3$	- Sn Mn(CO) ₅	150.4	3.4	A
$(C_6F_5)_2$	- Sn(C ₆ H ₅) ₂	149.6	3.0	A
$(C_6F_5)_2$	- Sn(C ₆ H ₅)Mn(CO) ₅	150.7	2.8	A
$(C_6F_5)_2$	- Sn[Mn(CO) ₅] ₂	151.6	2.7	A
C ₆ F ₅	- Sn(C ₆ H ₅) ₃	151.2	2.6	A
C ₆ F ₅	- Sn(C ₆ H ₅) ₂ Mn(CO) ₅	152.6	2.6	A
C ₆ F ₅	- Sn(CH ₃) ₃	153.5	1.9	B

^a
in ppm based on the scale: C₆F₆ = 163.0 upfield from CFC1₃

^b
in cps.

^c
A, this work: B, Reference (15).

TABLE XVI

Para-fluorine Chemical Shift (ϕ_p) and the Ortho-Para-Fluorine Coupling Constant (J_{24}) for Some Pentafluorobenzonitrile Complexes, and Other Compounds of Interest

	ϕ_p^a	J_{24}^b	Ref. ^c
C_6F_5 - $CNBCl_3$	136.0	8.5	A
C_6F_5 - $CNBF_3$	141.6	6.3	A
C_6F_5 - CN	143.2	5.8	A
C_6F_5 - $CNBBr_3$	146.9	4.6	A
C_6F_5 - SiF_3	143.4	6.6	B,C
C_6F_5 - CF_3	147.8	5.8	A
$[C_6F_5 - SFe(CO)_3]_2$	152.5	2.4	D
C_6F_5 - $SFe(CO)_2C_5H_5$	159.3	0	D

^ain ppm, based on the scale: C_6F_6 = 163.0 ppm upfield from $CFCl_3$.

^bin cps.

^cA, this work; B, Reference (18); C, Reference (34); D, Reference (33).

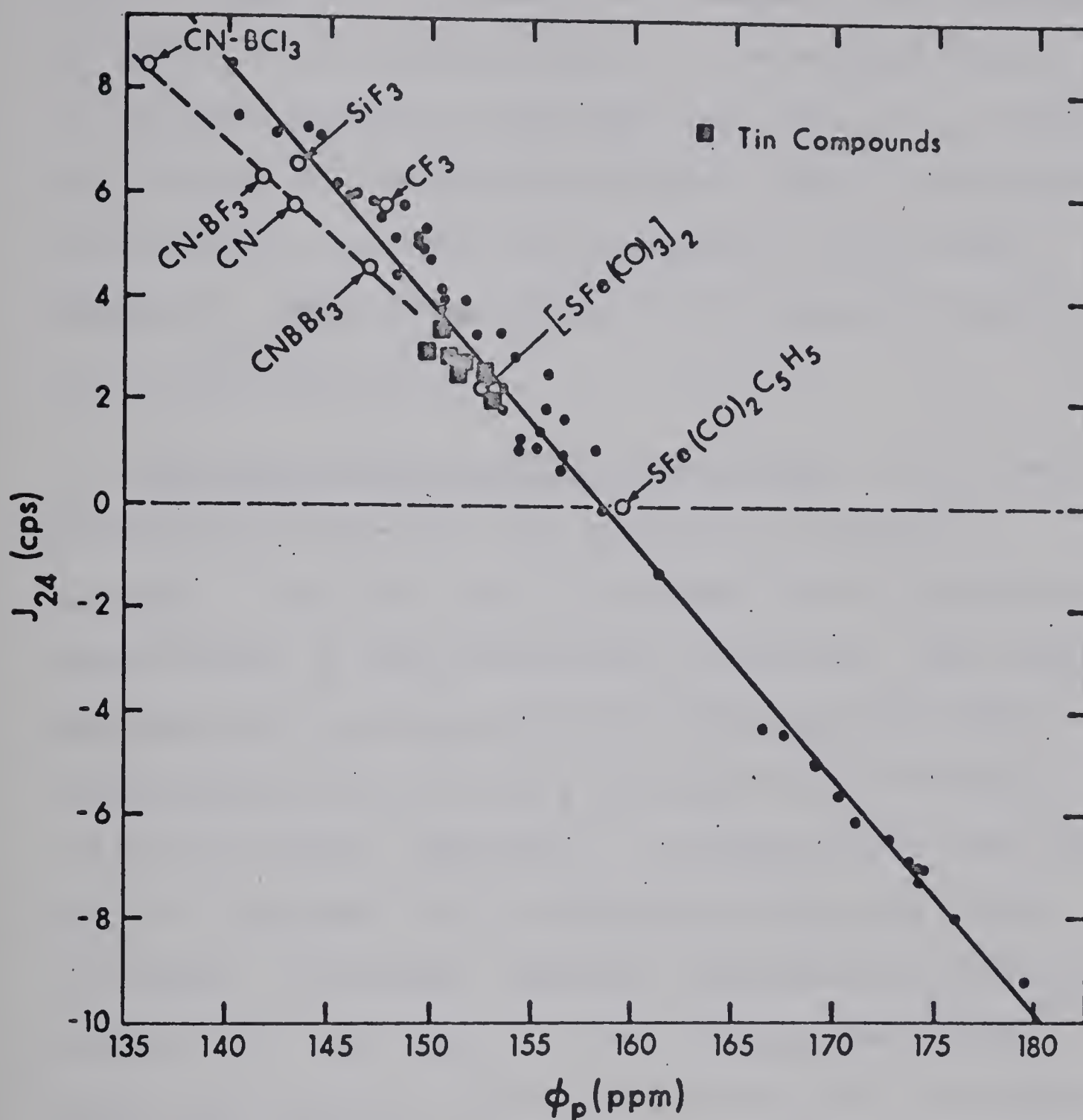


Figure 25. The $J_{24} - \phi_p$ relationship for various pentafluorobenzonitrile complexes, pentafluorophenyl tin derivatives, pentafluorothiophenoxy derivatives of iron carbonyl and pentafluorophenyl trifluorosilane and trifluoromethane.

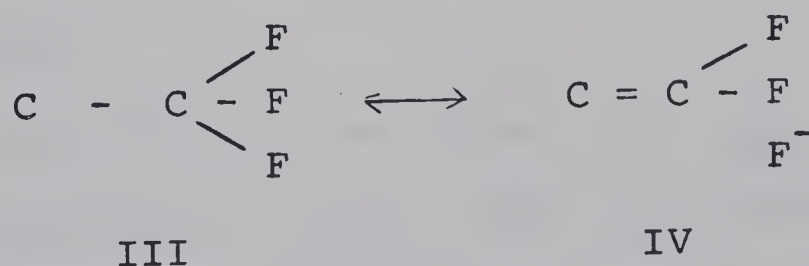
negligible π effect and is comparable to pentafluorothiophenol. This can be explained in terms of the lone pair on sulfur that normally donates to the benzene ring in II has been donated to the other iron atom in I. Hence the benzene ring experiences only the $(p \rightarrow d)$ π -withdrawal of the sulfur without its accompanying $(p \rightarrow p)$ π -donor character. This is analogous to the arguments applied in the phosphine series.

7. The pentafluorobenzonitrile complexes. It has been mentioned earlier that the $-\text{CN}$ group is a strong π acceptor. The lone pair on nitrogen can be donated to Lewis acids, in particular boron trihalides. The results of Table XVI and Figure 25 show that complexing pentafluorobenzonitrile with BF_3 increases the π withdrawal of the $-\text{CN}$ group. When BCl_3 , a stronger Lewis acid than BF_3 , is complexed, the π withdrawal of the $-\text{CN}$ group is further increased. However, complexing pentafluorobenzonitrile with BBr_3 , an even stronger Lewis acid, gives the anomalous result of decreasing the π acceptor properly to below that of the $-\text{CN}$ group itself.

As mentioned in Chapter II, the benzonitrile complexes were not isolated or characterized. Caution should therefore be applied to interpreting this interesting behavior. However the spectra showed that only one pentafluorophenyl species was present, with the sharpest peaks found in the course of this study;

these observations are themselves a partial characterization of the compounds.

8. The trifluoromethyl and trifluorosilyl groups. As noted earlier in this Chapter, the $-CF_3$ and $-SiF_3$ substituents lie close together in the π -acceptor region of the $J_{24} - \phi_p$ graph (Figure 25). This pair of substituents constitutes an exception to the general case in which substituents of first and second period elements are well separated on the graph which implies a π -acceptor capability for the $-CF_3$ group which is unusual in a first row element. The π -acceptor role of SiF_3 is readily understood in terms of the vacant 3d orbitals of silicon. A σ_R value of 0.14 has been given for the CF_3 group (68). This places it among the strongest π -acceptor groups in agreement with the result of the present work. This π -acceptor ability of the CF_3 group may be described in resonance terms as due to canonical forms such as the following:



The fluorine atoms would enhance the stability of form IV. An alternative description in molecular orbital terms (67) makes use of the vacant σ^* antibonding orbitals of the C-F bonds which are presumably lowered somewhat in energy by the highly electronegative fluorine atoms.

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APPENDIX A

FIRETC XLSQ2

```

C
C THIS IS A SPECIFIC PROGRAM FOR A LEAST SQUARE STRAIGHT LINE FIT
C BASED ON A UOI LSQ1 C/O DR PLAMBECK
C IN ADDITION THIS PROGRAMME WILL SELECT ITS VARIABLES FROM TWELVE
C SETS OF DATA AND WILL IDENTIFY EACH POINT BY NAME.
C THIS PROGRAMME WILL FIND COEFFICIENTS OF EQN. OF BEST STRAIGHT
C LINE IN  $Y = A(X_1 + K X_2) + \text{CONST}$  K WILL BE VARIED TO GIVE
C BEST COMBINATION OF  $X_1$  AND  $X_2$  .IF ONLY ONE SET OF X IS USED ,
C COEFFICIENTS OF  $Y = A X + B$  WILL BE FOUND.
C FIRST CARD -
C COLS. 1- 6 (I6) N = NUMBER OF POINTS TO BE ANALYSED
C 7-12 (I6) NLA = NO. OF SEARCHES REQD. TO FIND BEST K
C 13-18 (F6.2) ALOW = LOWER LIMIT OF 1ST SEARCH
C 19-24 (F6.2) AUP = UPPER LIMIT OF 1ST SEARCH
C 25-30 (I6) IX1 = FIELD NO. OF  $X_1$  DATA SET
C 31-36 (I6) IX2 = FIELD NO. OF  $X_2$  DATA SET
C IF ONLY 1 X SET IS TO BE USED IX1 = IX2
C 37-42 (I6) IY = FIELD NO. OF Y DATA SET
C 43-48 (F6.2) STARK = VALUE OF K ,IF THIS IS PREDETERMINED
C (IF THIS IS LEFT BLANK, PROGRAM WILL
C FIND BEST K )
C THEN FOLLOWS N CARDS , ONE PER POINT, ON WHICH IS STATED
C COLS. 1-3 REFERENCE (ALPHABETIC)
C COLS. 4-16 NAME OF POINT
C FIELD NO. 1 2 3 4 5 6 7 8 9 10 11 12
C D-O D-P D-M J24 J34 J23 J25 J26 J35 J12 J13 J14
C FORMAT (1X,A2,2A6,3F7.0,1X,F4.0,3F5.0,F4.0,4F5.0)
C FOR FURTHER INFO. SEE M. HOGREN
C
C DIMENSION A(20,15), B(20,4), X(100), Y(100,4), W(100), SUM(4),
X RESID(100,4), STD(15,4), EVAL(100),
X NAME1(100), NAME2(100),NAMREF(100),D(4),
X XA(100),YA(100),CJ24 (100),CJ23(100),GOF(99),
X DO(100),DP(100),DM(100),CJ24(100), CJ25(100),CJ26(100),
X CJ35(100),CJ12(100),CJ13(100),CJ14(100)
X ,X1A(100),X2A(100),XI(100),YI(100),NAM(6)
C DATA NAM(1)/6HB GOOD/,NAM(2)/6H GOOD/,NAM(3)/6H FAIR/,NAM(4)/6H
X POOR/,NAM(5)/6H BAD/,NAM(6)/6H FURAR/
1 READ(5,1000) N, NLA, ALOW, AUP,IX1,IX2,IY,STARK
IF(N) 1,1,2
2 DO 260 I = 1,N
READ (5,2000) NAMREF(I),NAME1(I),NAME2(I),DO(I),DP(I),DM(I),CJ24(
XI),CJ34(I), CJ23(I),CJ25(I),CJ26(I),CJ35(I),CJ12(I),
XCJ13(I),CJ14(I)
GO TO (201,202,203,204,205,206,207,208,209,210,211,212) ,IX1
201 X1A(I) = DO(I)
GO TO 220
202 X1A(I) = DP(I)
GO TO 220
203 X1A(I) = DM(I)
GO TO 220
204 X1A(I) = CJ24(I)
GO TO 220
205 X1A(I) = CJ34(I)
GO TO 220
206 X1A(I) = CJ23(I)
GO TO 220
207 X1A(I) = CJ25(I)
GO TO 220

```



```
208 X1A(I) = CJ26(I)
GO TO 220
209 X1A(I) = CJ35(I)
GO TO 220
210 X1A(I) = CJ12(I)
GO TO 220
211 X1A(I) = CJ13(I)
GO TO 220
212 X1A(I) = CJ14(I)
220 GO TO (221,222,223,224,225,226,227,228,229,230,231,232) ,IX2
221 X2A(I) = DO(I)
GO TO 240
222 X2A(I) = DP(I)
GO TO 240
223 X2A(I) = DM(I)
GO TO 240
224 X2A(I) = CJ24(I)
GO TO 240
225 X2A(I) = CJ34(I)
GO TO 240
226 X2A(I) = CJ23(I)
GO TO 240
227 X2A(I) = CJ25(I)
GO TO 240
228 X2A(I) = CJ26(I)
GO TO 240
229 X2A(I) = CJ35(I)
GO TO 240
230 X2A(I) = CJ12(I)
GO TO 240
231 X2A(I) = CJ13(I)
GO TO 240
232 X2A(I) = CJ14(I)
240 GO TO (241,242,243,244,245,246,247,248,249,250,251,252) ,IY
241 YA(I) = DO(I)
GO TO 260
242 YA(I) = DP(I)
GO TO 260
243 YA(I) = DM(I)
GO TO 260
244 YA(I) = CJ24(I)
GO TO 260
245 YA(I) = CJ34(I)
GO TO 260
246 YA(I) = CJ23(I)
GO TO 260
247 YA(I) = CJ25(I)
GO TO 260
248 YA(I) = CJ26(I)
GO TO 260
249 YA(I) = CJ35(I)
GO TO 260
250 YA(I) = CJ12(I)
GO TO 260
251 YA(I) = CJ13(I)
GO TO 260
252 YA(I) = CJ14(I)
260 CONTINUE
KX = 11
IF (IX2.EQ.IX1) GO TO 115
```



```

      IF (SIARK) 116,112,116
116 XAK = STARK
      GO TO 114
115 XAK = 0.0
      STARK = 0.0
114 KX = 1
112 CONTINUE
      DO 130 LA = 1,NLA
      IF (KX.EQ.1) GO TO 118
      DELK = (AUP - ALOW)/10.0
      WRITE (6,2010) LA,ALOW,AUP,DELK
118 CONTINUE
      DO 110 K = 1,KX
      IF (KX.EQ.1) GO TO 119
      XAK = (FLOAT(K-1))*DELK + ALOW
119 CONTINUE
113 DO 111 I=1,N
111 XA(I) = X1A(I) + XAK*X2A(I)
      SUMXY = 0.0
      SUMX = 0.0
      SUMY = 0.0
      SUMXX = 0.0
      SUMYY = 0.0
      DO 120 I = 1,N
      SUMXY = SUMXY + XA(I)*YA(I)
      SUMX = SUMX + XA(I)
      SUMY = SUMY + YA(I)
      SUMXX = SUMXX + XA(I)*XA(I)
120 SUMYY = SUMYY + YA(I)*YA(I)
      G = N
      GOF(K)=1.0-(((G*SUMXY-SUMX*SUMPY)**2)/((G*SUMXX-SUMX**2)*(G*SUMPY-
      XSUMY**2)))
      IF(KX .EQ. 1) GO TO 150
110 WRITE (6,2020) XAK,GOF(K)
      AA = GOF(1)
      DO 140 NA = 1,11
      IF (AA-GOF(NA)) 140,140,145
145 AA = GOF(NA)
      JA = NA
140 CONTINUE
      KSTAR = JA
      STARK = (FLOAT(KSTAR-1))*DELK + ALOW
      WRITE (6,2030) STARK
      IF (LA.EQ.NLA) GO TO 150
      ALOW = STARK - DELK
130 AUP = STARK + DELK
150 CONTINUE
180 DO 160 I=1,N
      W(I) = 1.0
      Y(I,1) = YA(I)
160 X(I) = X1A(I) + STARK*X2A(I)
      M = 2
      L = 1
      IEVAL = 1
      5 CALL LSQ1(X,Y,W,RESID,N,SUM,L,A,R,M)
      DEG = N - M - 1
      DO 6 I = 1,M
      DO 6 J = 1,L
      6 STD(I,J) = SQRT(SUM(J) * A(I,I)/DEG)
      WRITE (6,3000) N,M,N1,L,NLA,STARK

```



```

DO 7 I = 1,M
7 WRITE (6,4000) (A(I,J), J = 1,M)
DO 8 J = 1,L
WRITE (6,5000) (R(I,J), STD(I,J), I = 1,M)
WRITE (6,6000) SUM(J)
D(J) = SQRT((SUM(J))/(FLOAT(N)))
WRITE (6,6100) D(J)
DA = 0.0
DO 25 I = 1,N
25 DA = DA + SQRT(RESID(I,J)**2)
DB = DA/FLOAT(N)
WRITE (6,6200) DB
IF(KX .EQ.11) GO TO 26
KSTAR = 1
26 CONTINUE
IF (GOF(KSTAR).LE.0.01) GO TO 40
IGOF = INT(GOF(KSTAR)*10.0) + 1
GO TO (41,42,43,44,44,45,45,45,45,45), IGOF
40 NAMGOF = NAM(1)
GO TO 46
41 NAMGOF = NAM(2)
GO TO 46
42 NAMGOF = NAM(3)
GO TO 46
43 NAMGOF = NAM(4)
GO TO 46
44 NAMGOF = NAM(5)
GO TO 46
45 NAMGOF = NAM(6)
46 WRITE (6,6300) GOF(KSTAR),NAMGOF
IF (STARK) 21,20,21
20 WRITE (6,8600) B(2,J),B(1,J)
GO TO 22
21 STARKB = STARK*B(2,J)
WRITE (6,8500) B(2,J),STARKB,B(1,J)
22 CONTINUE
WRITE (6,2100) IY,IX1,IX2
IF (IEVAL) 8,8,9
9 DO 10 I = 1,N
10 EVAL(I) = RESID(I,J) + Y(I,J)
WRITE (6,7000) (X(I), Y(I,J),EVAL(I),RESID(I,J),
XNAME1(I),NAME2(I), I = 1,N)
WRITE (6,7100) (NAMREF(I),NAME1(I),NAME2(I),
X DO(I),DP(I),DM(I),CJ24(I),CJ34(I),CJ23(I)
X CJ25(I),CJ26(I),CJ35(I),CJ12(I),CJ13(I),CJ14(I), I = 1,N)
WRITE (3,7500) (X(I),Y(I,J), I = 1,N)
WRITE (3,9500)
NPT = N
DO 30 I = 1,N
XI(I) = X(I)
30 YI(I) = Y(I,J)
LINE = 0
XPIN = 0.0
XPNC = 0.0
YPIN = 0.0
YPNC = 0.0
CALL GRAPH (NPT,XI,YI,LINE,XPIN,YPIN,YPNC,XPNC)
8 WRITE (6,9000)
GO TO 1
1000 FORMAT (2I6,2F6.0,3I6,F6.2)

```



```

2000 FORMAT (1X,A2,2A6,1X,F6.0,2F7.0,1X,F4.0,3F5.0,F4.0,4F5.0)
2010 FORMAT (54H -----,
X      6HJ NO.13,28H SEARCH FOR BEST VALUE OF K /
X      18HJ LOWER LIMIT =F10.5/18H UPPER LIMIT =F10.5/
X      18H INTERVAL =F10.5)
2020 FORMAT (6HJ K =F10.5,19H CRITERIA OF FIT = 1PF13.5)
2030 FORMAT (12HJ BEST K = F9.5)
2100 FORMAT ( 16HJ VARIABLES USED / 7H Y = 13/ 7H X1A = 13 /
X      7H X2A = 13 )
3000 FORMAT (48H1 LEAST SQUARE POLYNOMIAL FIT USING LSQ1 /
X      3HJN=13.5H M=12.6H N1=12.5H L=12.6H NLA =12.10H FINA
XL K =1PF13.6/ 13HJERROR MATRIX)
4000 FORMAT (1HJ1P8E14.5)
5000 FORMAT (37HJ COEFFICIENT ERROR/(1H 1P2E20.7))
6000 FORMAT (36HJWEIGHTED SUM OF SQUARED DEVIATIONS=1PF13.5)
6100 FORMAT (23HJ ROOT MEAN SQUARE =1PF13.5)
6200 FORMAT (19HJMEAN DEVIATION IS F10.5)
6300 FORMAT (19HJCRITERIA OF FIT = F9.6/48H WHICH MEANS APPROXIMATION T
XO STRAIGHT LINE WAS A6)
7000 FORMAT ( 62HJ X Y EVALUATION RESIDUAL ID
XENTITY /(1H 4F12.4,2X,2A6))
7100 FORMAT ( 95H1
XREF IDENTITY D-OR D-PA D-ME J24 J34 J23 J25 J
X26,J35 J12 J13 J14 /
X (3X,1A2, 2A6,1X,F7.2,1X,F7.2,1X,F7.2,2X,
X F4.1,1X,F5.1,1X,F5.1,1X,F5.1,1X,F4.1,1X,F5.1,1X,F5.1,1X,
X F5.1,1X,F5.1))
7500 FORMAT (1X,2E20.7)
8500 FORMAT (19HJFINAL EQUATION IS /
X 4H Y =F9.4 .7H X1A + F9.4.6H X2A + F9.4/6HJWHERE )
8600 FORMAT (19HJFINAL EQUATION IS /
X4H Y =F9.4.5H X + F9.4/6HJWHERE)
9000 FORMAT (54H1- - - - -)
9500 FORMAT (4H END)
END

```

\$IBFTC XLSQ1

```

C
SUBROUTINE LSQ1(X,Y,W,RESID,N,SUM,L,A,B,M)
C
DIMENSION X(500),Y(500,1),RESID(500,1),A(20,15),B(20,1),C(500,15),
XSUM(1),W(500)
C
COMMON C
C
DO 1 I = 1,N
1 C(I,1) = 1.0
DO 2 J = 2,M
DO 2 I = 1,N
2 C(I,J) = C(I,J - 1) * X(I)
DO 3 I = 1,M
DO 3 J = 1,M
A(I,J) = 0.0
DO 3 K = 1,N
3 A(I,J) = A(I,J) + C(K,I) * C(K,J) * W(K)
DO 4 J = 1,L
DO 4 I = 1,M
B(I,J) = 0.0
DO 4 K = 1,N
4 B(I,J) = B(I,J) + C(K,I) * Y(K,J) * W(K)
CALL MATINV (A,M,B,L,DETERM)

```



```

DO 6 J = 1,L
SUM(J) = 0.0
DO 6 I = 1,N
RESID(I,J) = POLY(X(I),M,R,J,20,1) - Y(I,J)
6 SUM(J) = SUM(J) + RESID(I,J)**2*W(I)
RETURN
END

```

SIRFIC XMATIN

C
C MATRIX INVERSION WITH ACCOMPANYING SOLUTION OF LINEAR EQUATIONS
C

SUBROUTINE MATINV(A,N,B,M,DETERM)

C
C DIMENSION IPIVOT(20), A(20,20), B(20,1), INDEX(20,2), PIVOT(20)
C COMMON PIVOT,INDEX, IPIVOT
C EQUIVALENCE (IROW,JROW), (ICOLUMN,JCOLUMN), (AMAX,T,SWAP)

C
C INITIALIZATION
C

DETERM = 1.0
DO 20 J = 1,N
20 IPIVOT(J) = 0
DO 550 I = 1,N

C
C SEARCH FOR PIVOT ELEMENT
C

AMAX = 0.0
DO 105 J = 1,N
IF (IPIVOT(J) - 1) 60,105,60
60 DO 100 K = 1,N
IF (IPIVOT(K) - 1) 80,100,740
80 IF (ABS(AMAX) - ABS(A(J,K))) 85,100,100
85 IROW = J
ICOLUMN = K
AMAX = A(J,K)
100 CONTINUE
105 CONTINUE
IPIVOT(ICOLUMN) = IPIVOT(ICOLUMN) + 1

C
C INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL
C

IF (IROW - ICOLUMN) 140,260,140
140 DETERM = -DETERM
DO 200 L = 1,N
SWAP = A(IROW,L)
A(IROW,L) = A(ICOLUMN,L)
200 A(ICOLUMN,L) = SWAP
IF (M) 260,260,210
210 DO 250 L = 1,M
SWAP = B(IROW,L)
B(IROW,L) = B(ICOLUMN,L)
250 B(ICOLUMN,L) = SWAP
260 INDEX(I,1) = IROW
INDEX(I,2) = ICOLUMN
PIVOT(I) = A(ICOLUMN,ICOLUMN)
DETERM = DETERM * PIVOT(I)

C
C DIVIDE PIVOT ROW BY PIVOT ELEMENT
C

A(ICOLUMN,ICOLUMN) = 1.0


```

DO 350 L = 1,N
350 A(ICOLUM,L) = A(ICOLUM,L)/PIVOT(I)
IF (M) 380,380,360
360 DO 370 L = 1,M
370 B(ICOLUM,L) = B(ICOLUM,L)/PIVOT(I)

```

C
C REDUCE NONPIVOT ROWS

```

C
380 DO 550 L1 = 1,N
IF (L1 - ICOLUM) 400,550,400
400 T = A(L1,ICOLUM)
A(L1,ICOLUM) = 0.0
DO 450 L = 1,N
450 A(L1,L) = A(L1,L) - A(ICOLUM,L) * T
IF (M) 550,550,460
460 DO 500 L = 1,M
500 B(L1,L) = B(L1,L) - B(ICOLUM,L) * T
550 CONTINUE

```

C
C INTERCHANGE COLUMNS

```

C
DO 710 I = 1,N
L = N + 1 - I
IF (INDEX(L,1) - INDEX(L,2)) 630,710,630
630 JROW = INDEX(L,1)
JCOLUM = INDEX(L,2)
DO 705 K = 1,N
SWAP = A(K,JROW)
A(K,JROW) = A(K,JCOLUM)
A(K,JCOLUM) = SWAP
705 CONTINUE
710 CONTINUE
740 RETURN
END

```

\$IBFTC XPOLY

```

REAL FUNCTION POLY(X,M,COEFF,J,MR,MC)
DIMENSION COEFF(MR,MC)
POLY = 0.0
DO 1 N = 1,M
MA = M - N + 1
1 POLY = POLY * X + COEFF(MA,J)
RETURN
END

```

\$IBFTC GRAPH

```

SUBROUTINE GRAPH(NPT,XI,YI,LINE,XPIN,XPNC,YPIN,YPNC)
DIMENSION XI(501),YI(501), X(501),Y(501),G(104),YC(11)
DATA BL/1H /,AA/1H*/,PER/1H./,AX/1HX/
XMIN=XPIN
XINC=XPNC
YMIN=YPIN
YINC=YPNC
B=-1.0E+25
MB=0
DO 2 I=1,NPT
A=1.0E+25
MA=0
DO 1 J=1,NPT
IF (XI(J).GT.A.OR.XI(J).LT.B.OR.XI(J).EQ.B.AND.J.GE.MB) GO TO 1
A=XI(J)
MA=J
2

```



```

1 CONTINUE
  X(I)=A
  Y(I)=YI(MA)
  B=A
2 MB=MA
  NLN=LINE
  IF (LINE.EQ.0) NLN=50
  IF (LINE.GT.150) NLN=150
  IF (XINC.EQ.0.0) CALL SCALE(NLN,NPT,X,XMIN,XINC,XAS,MPX,0)
  IF (YINC.EQ.0.0) CALL SCALE(100,NPT,Y,YMIN,YINC,YAS,MPY,1)
  DO 3 I=1,11
3 YC(I)=YMIN+FLOAT(I-1)*YINC*10.0
  WRITE (6,901) MPX,XAS,MPY,YAS,YC
  NLN=NLN+1
  MA=1
  Q=AA
  DO 12 I=1,NLN
  DO 4 J=2,104
4 G(J)=0
  G(1)=AA
  IF (10*((I-1)/10).NE.I-1) GO TO 8
  DO 110 J=1,101,10
110 G(J)=PER
  8 IF (MA.GT.NPT) GO TO 10
  II=(X(MA)-XMIN+0.5*XINC)/XINC+1.0
  IF (II.GT.1) GO TO 10
  IF (II.LT.1) GO TO 9
  JJ=(Y(MA)-YMIN+0.5*YINC)/YINC+1.0
  IF (JJ.GT.0.AND.JJ.LT.102) G(JJ)=AX
  9 MA=MA+1
  GO TO 8
10 IF (10*((I-1)/10).NE.I-1) GO TO 11
  A=XMIN+FLOAT(I-1)*XINC
  WRITE (6,902) A,G
  GO TO 12
11 WRITE (6,903) G
12 Q=BL
  RETURN
901 FORMAT (1H1 //27X,7HABCISSA,13,E18.8,5X,8HORDINATE,13,E18.
18//5X,11F10.3)
902 FORMAT (1X,F10.3,104A1)
903 FORMAT (11X,104A1)
END

```

\$IBFIC SCALE

```

SUBROUTINE SCALE(NLN,NPT,Y,YMIN,YINC,YAS,MPY,ITP)
DIMENSION Y(501),SINC(6)
DATA SINC/1.0,2.0,2.5,4.0,5.0,10.0/
MPY=0
YAS=0.0
FLN=NLN
YMIN=Y(1)
YMAX=Y(NPT)
IF (ITP.EQ.0) GO TO 101
DO 1 I=1,NPT
  IF (Y(I).GT.YMAX) YMAX=Y(I)
  IF (Y(I).LT.YMIN) YMIN=Y(I)
1 CONTINUE
101 YINC=(YMAX-YMIN)/FLN
  MA=-ALOG10(YINC)
  IF (YINC.LT.1.0) MA=MA+1

```



```

YINC=YINC*10.0**MA
DO 2 I=1,6
  IF (YINC.LE.SINC(I)) GO TO 3
2 CONTINUE
3 YINC=SINC(I)*0.1**MA
  IF (ABS(YMIN).LT.10000.0.AND.ABS(YMAX).LT.10000.0) GO TO 102
  MA=-ALOG10(ABS(YMIN))
  IF (ABS(YMAX).GT.ABS(YMIN)) MA=-ALOG10(ABS(YMAX))
  YMIN=YMIN*10.0**MA
  YMAX=YMAX*10.0**MA
  YINC=YINC*10.0**MA
  MPY=-MA
103 IF (YMIN.LT.0.0.AND.ABS(YMIN).LT.0.5*YINC) YMIN=0.0
  YCMN=FLOAT(IFIX(YMIN*1.0000001/YINC))*YINC
  IF (YMIN.LT.0.0.AND.YCMN.GT.YMIN) YCMN=YCMN-YINC
  YCMN=YCMN*0.1
  YTIN=YMIN
  DO 4 I=1,100
  YMIN=FLOAT(IFIX(YCMN*1.0000005*10.0**I))*0.1**(I-1)
  IF (YCMN.GE.0.0) GO TO 203
  IF (YMIN.GT.YTIN*.9999998) YMIN=YMIN-0.1**(I-1)
203 IF (YMIN+YINC*ELN.GE.YMAX*0.9999998) GO TO 5
  4 CONTINUE
  5 YMAX=YMIN+YINC*ELN
10 IF (ABS(YMIN).LT.10000.0.AND.ABS(YMAX).LT.10000.0) GO TO 11
  YMIN=YMIN*0.1
  YINC=YINC*0.1
  YMAX=YMAX*0.1
  MPY=MPY+1
  GO TO 10
11 IF (YINC.GE.0.001.AND.YINC.NE.0.0025) GO TO 14
12 YMIN=YMIN*10.0
  YINC=YINC*10.0
  YMAX=YMAX*10.0
  MPY=MPY-1
  IF (ABS(YMIN).LT.10000.0.AND.ABS(YMAX).LT.10000.0) GO TO 11
  IF (YINC.LT.0.001.OR.YINC.EQ.0.0025) GO TO 12
  X=ABS(YMAX)
  IF (X.LT.ABS(YMIN)) X=ABS(YMIN)
  YAS=(FIX((X-10000.0)*0.001)+1)*1000
  YMIN=YMIN-YAS
14 DO 15 I=1,NPT
15 Y(I)=Y(I)*0.1**MPY-YAS
  RETURN
  END

```


APPENDIX B

Table^a giving values of the correlation coefficient, (r_{xy}) , which have certain probabilities of being exceeded for observations of variables whose parent distributions are independent.

To illustrate: for a sample of 10 pairs of unrelated variables, the probability is 0.10 that it will have $(r_{xy}) \geq 0.549$.

N	Probability			
	0.10	0.05	0.01	0.001
3	0.988	0.997	1.000	1.000
5	0.805	0.878	0.959	0.992
7	0.669	0.754	0.874	0.951
10	0.549	0.632	0.765	0.760
15	0.441	0.514	0.641	0.760
30	0.307	0.362	0.464	0.572
60	0.219	0.259	0.337	0.422
100	0.168	0.199	0.259	0.327

^a
Adapted from Table V , Reference (32) .

APPENDIX C

Table of Hammett Functions, σ_{para} and σ_{meta} ; and of Taft Functions, $\sigma_{\text{R}}^{\text{O}}$ and σ_{I} , for Certain Organic Substituents.

Substituent	$\sigma_{\text{para}}^{\text{a}}$	$\sigma_{\text{meta}}^{\text{a}}$	$\sigma_{\text{R}}^{\text{O}^{\text{b}}}$	$\sigma_{\text{I}}^{\text{c}}$
CN	0.66	0.56	0.02	0.58
CF ₃	0.54	0.43	0.41
CO ₂ H	0.41	0.35	0.30
I	0.28	0.35	-0.12	0.39
H	0.00	0.00	0.00	0.00
Br	0.23	0.39	-0.19	0.45
Cl	0.23	0.37	-0.20	0.47
CH ₃	-0.17	-0.07	-0.10	-0.05
SH	0.15	0.25	0.25
OH	-0.37	0.12	-0.40	0.25
NH ₂	-0.66	-0.16	-0.48	0.10

a Reference (52)

b Reference (47)

c Reference (48)

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